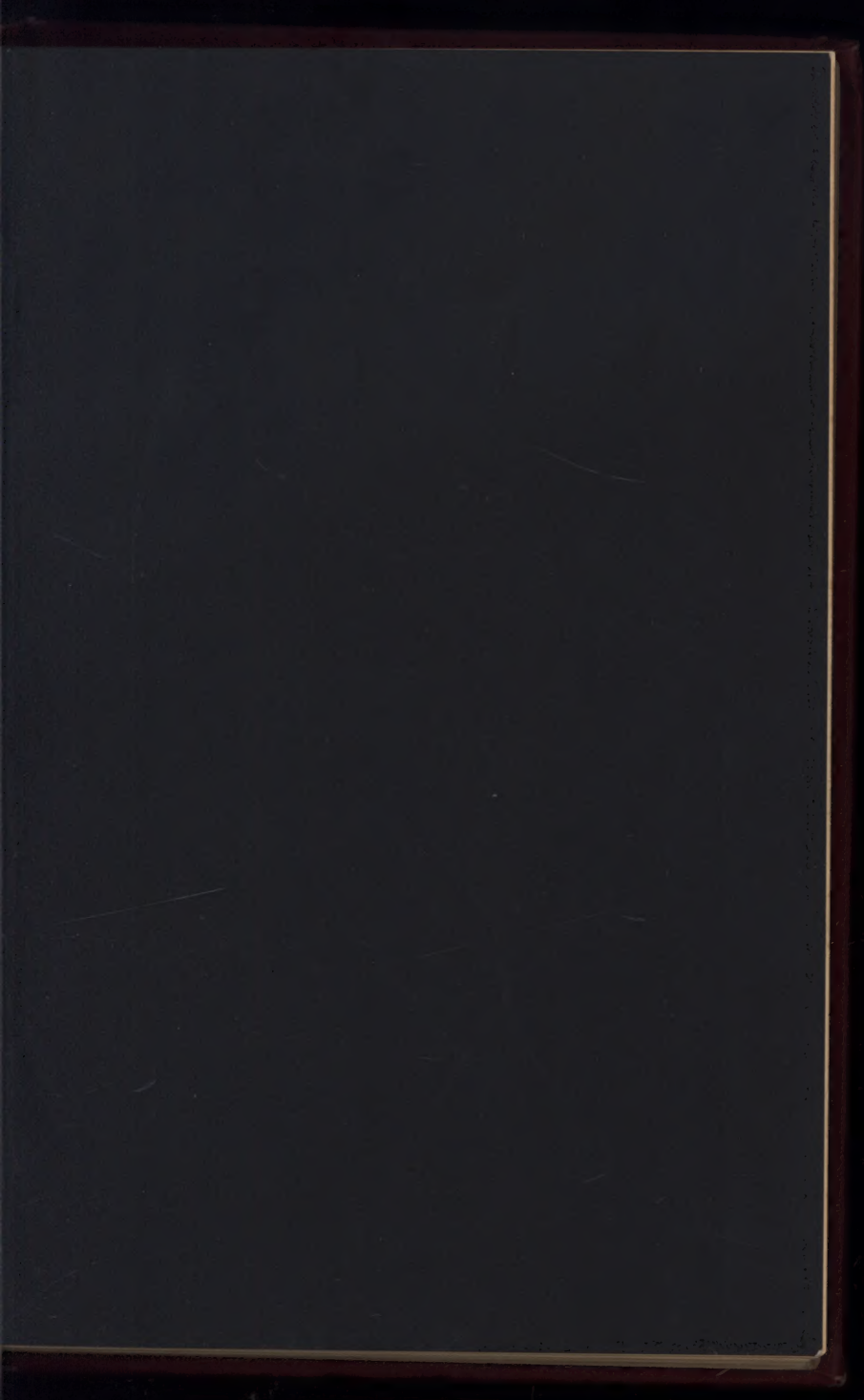
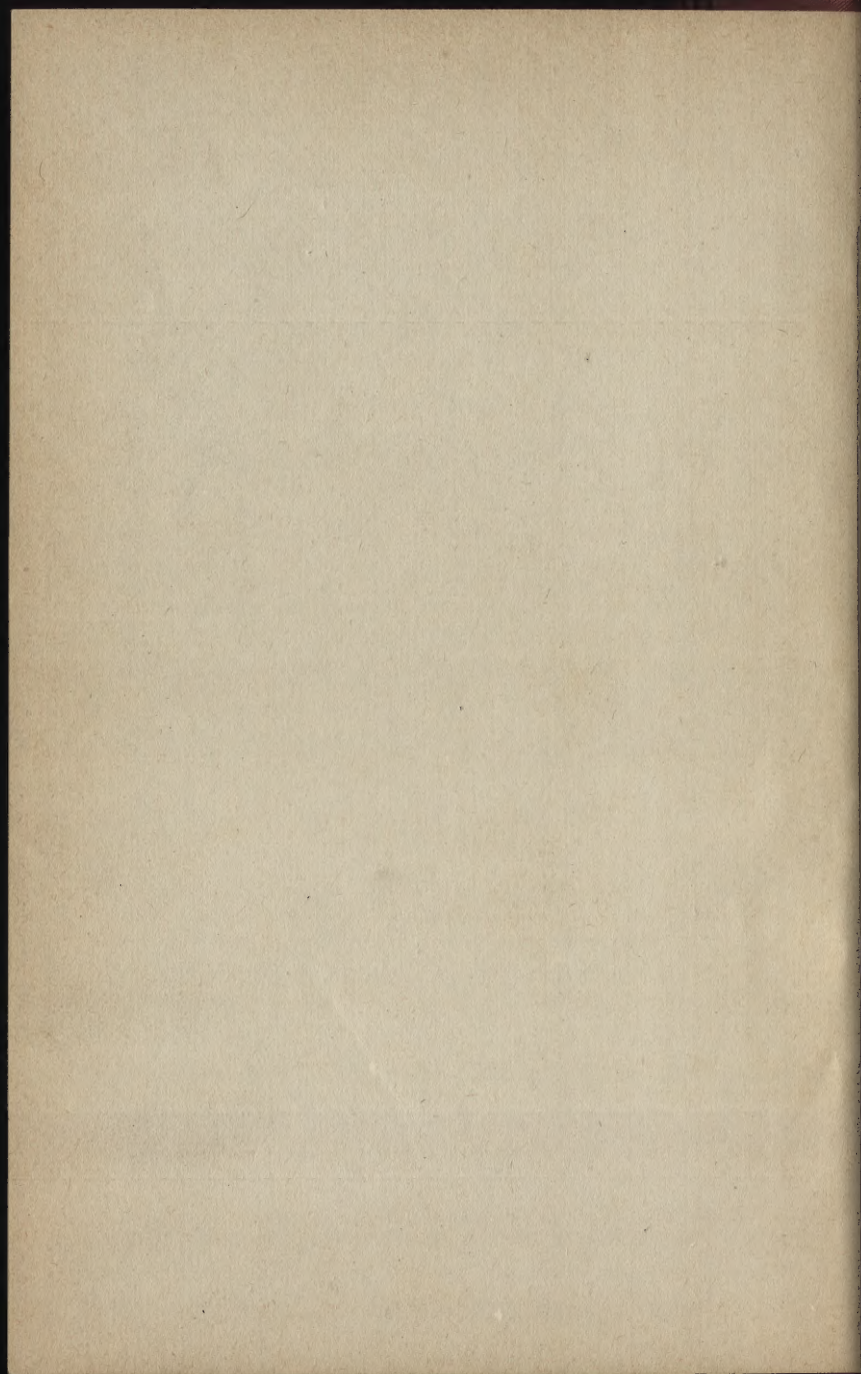


POTTERY DECORATING

R. HAINBACH





Pottery

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POTTERY DECORATING

A DESCRIPTION OF ALL THE PROCESSES FOR
DECORATING POTTERY AND PORCELAIN

BY

RUDOLF HAINBACH

TRANSLATED FROM THE GERMAN

BY CHAS. SALTER

WITH TWENTY-TWO ILLUSTRATIONS

LONDON

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"THE POTTERY GAZETTE" OFFICES

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PREFACE

WHEREAS the methods of manufacturing the body for the finest ceramic ware, namely, fine earthenware, hard and soft porcelain, have attained the highest stage of development during the past half-century, the methods relating to the artistic decoration of the ware are still in process of evolution—probably because chemical science is now in an advanced condition and scarcely a day passes without some new discovery in the domain of chemical technology.

Ceramists are constantly endeavouring to produce new colour effects on their ware, and combine these with effects of reflection and lustre; and surprising results have been obtained in the decoration of ceramic products with iridescent colours, lustres, and the noble metals. The high state of the transfer printing method applied to glazed ware has enabled articles to be put on the market, decorated in a highly artistic manner and at prices out of all proportion to those which must be paid for ware of identical appearance that has been produced by hand.

Photography, too, has now been pressed into the service of the ceramist and has enabled perfect photographic pictures to be reproduced on porcelain, the results surpassing all other methods in durability.

The author has also succeeded in applying the sand blast—previously confined to the glass industry—to the decoration

of porcelain, and in combining this process with electroplating for the decoration of ceramic objects.

In accordance with the title selected for the present work, the author has set himself the task of describing all the methods of ceramic decoration, by means of glazes, engobes, colours, metals, and lustres, in a manner that will enable any professional ceramist to obtain any desired effect in this class of decoration.

Special consideration has also been devoted to describing the methods of preparing the glazes, etc., in such a way that failure is impossible if the instructions given are carefully followed. The author therefore is filled with the pleasant hope that his work will be found a reliable handbook and work of reference on all practical questions in connection with its subject.

THE AUTHOR.

1907.

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POTTERY DECORATING

PART I.

INTRODUCTION.

GLAZES AND ENGOBES.

THE attempt at shaping plastic materials into the form of vessels and utensils was the first symptom of industrial activity evinced by man in the course of his intellectual development. Since the clay occurring in great abundance on various parts of the earth's surface exhibits the property of forming an unusually plastic mass when mixed with water, and setting hard again when dried, it is highly probable that the first vessels made were of this material. The circumstance that vessels made solely of clay are extremely fragile will sufficiently account for the absence of any existing remains of these products at the present time.

Accident may have taught man that exposure to a red heat will convert clay into a hard, resistant body: and it is to the discovery of this fact that we owe the existence of numerous souvenirs of clay modelling dating from prehistoric times. The remains of the lake dwellers' habitations always contain, in addition to fragments of textiles and weapons of

horn and stone, vessels of more or less well-burned clay in a good state of preservation.

In proportion as civilisation developed, the art of making clay vessels advanced to higher stages. Thus we find in ancient Assyrian buildings beautifully coloured bricks in general use for decorative purposes; and the Egyptians had already learned the art of making earthenware vessels in different colours and coating them with glaze. Among the ancient Greeks and Etruscans the potter's trade reached the dignity of a fine art. The handsome vases of Grecian and Etruscan origin that adorn our museums afford striking testimony that these peoples had brought this branch of human artistic skill to a height that compels our admiration at the present day.

As the civilisation of the antique world declined, the art of the potter, like all the other arts, receded to a low ebb, and it was only about the eighth century of our era that it began to flourish once more, this time more particularly in the hands of the Moors in Spain. Coloured and glazed pottery by Moorish artists of that age testify eloquently to the high position they had attained in this branch of art; and it is probably due to their influence that potting had risen from a mere handicraft to a fine art in Italy by the fifteenth century.

A Florentine artist, Luca della Robbia, was the first to produce the highly appreciated glazed and painted artistic earthenware known as "Majolica," specimens of which are numbered among the costly treasures of our museums. Luca della Robbia and his successors already understood the art of coating pottery with various glazes, and of applying to the latter a diversity of colours; so that we must regard this artist as the real father of modern ceramics. The production of majolica ware spread throughout Italy, and works were established at Pesaro, Urbino, and other places, for turning out

glazed and painted earthenware. Faenza was also a seat of the industry; and the name "Faience," given to pottery ware possessing certain qualities, is derived from that town.

The development of potting was also accompanied by progress in the ceramic art in Germany, France, and the Netherlands. There is no doubt that the ceramists of these countries were disciples of the Italian masters, especially as regards the beauty of their glazes and colours; but it should also be mentioned that German pottery had reached a high state of perfection even before the introduction of majolica ware. Germany and the Netherlands manufactured a kind of ware distinguished by extreme hardness and strength—a product still occupying an important position among ceramic products, under the name of "stoneware."

In England, potting remained for a long period in the state of a mere handicraft, the potters only turning out simple ware, suitable for domestic purposes, and it was not until the middle of the eighteenth century that the ceramic art took a sudden upward turn in this country, when Josiah Wedgwood succeeded in making ware of such eminent beauty, both in glaze and colour, that it rapidly acquired a world-wide reputation. It was to Wedgwood also that we owe the production of "Queen's ware," characterised by a uniform pure whiteness throughout the mass.

Although European ceramics had attained a high state of development, the art was still several centuries behind that of Eastern Asia, none of the Western makers being able to produce ware able to compare in beauty and strength with that imported, under the name of "porcelain," from China and Japan. There was no lack of endeavour to produce a porcelain body equal in its properties to that of the Chinese potters, but the results were not crowned with any great success, until Johann Friedrich Böttcher, in 1709, prepared a body equal to that of Chinese porcelain.

The rapid extension of this new method of manufacture, contemporaneously with the great strides made by chemistry at the close of the eighteenth century, enabled European porcelain to overtake the Chinese product, both in point of internal properties and colouring; but it was reserved for the nineteenth century to raise the porcelain industry to its present high position. This result was obtained only after innumerable painstaking experiments on the composition of the porcelain bodies, glazes, and appropriate pigments—experiments necessitating the prosecution of exact chemical investigations as an essential preliminary to success.

These investigations were not confined solely to porcelain, but extended to other branches of ceramics as well. Whereas formerly, in the production of ordinary pottery ware, each maker worked in accordance with the teachings of practical experience, and modified the operations to suit the raw material available, it became the practice to subject the chemical composition of the materials—more particularly the clays and the substances employed for glazes—to exhaustive examination; and this has now been pushed so far that attention is bestowed on the chemical properties and behaviour in the kiln, etc., of the clay used for making even the commonest class of ware—namely, bricks.

In addition to carefully testing the clay forming the fundamental substance of all ceramic labours, it was found advisable to examine the substances used in preparing the glazes, experience having shown that, in order to ensure successful glazing, the substance of the ware must bear a certain relation to that of the glaze. This applies equally to the pigments used, whether these be incorporated with the body or glaze, or applied to the surface of the latter.

Unless the requisite relation be maintained between the fundamental substance of the ware and the applied coatings—which may be divided into two main categories, glazes and engobes—

the production of a perfect article will be solely a matter of chance, and the majority of the pieces will be more or less impaired by defects which we shall consider in detail later. In view of this fact it becomes essential for every ceramist to study most carefully the relation between the different components—shard, engobe, and glaze, or shard and glaze only—going to make the complete ware, so that he may be in a position to turn out a perfect article and to remedy any defects that may arise.

CHAPTER I.

GLAZES AND ENGOBES GENERALLY.

BY the term glaze we understand in ceramics a thin vitreous coating that attaches itself firmly to the body of the ware, in order to render the latter impervious to moisture, and impart a gloss and smoothness to the surface.

In the majority of instances the glaze is colourless, so that the colour of the underlying body shows through. Occasionally, however, the glaze is intentionally mixed with pigments or with substances rendering it more or less opaque, in which event the colour of the shard is no longer visible.

In addition to glazes, earthenware is sometimes coated with engobes, consisting of coloured clay, for the purpose of covering the surface of the ware with a coloured layer of predetermined thickness. These engobes are analogous in composition to the body of the ware, differing therefrom mainly in respect of colour.

Considerable importance also attaches to the coloured fluxes, which are closely allied to the glazes, inasmuch as their composition resembles that of the colourless glazes in many respects, though differing essentially in containing an admixture of pigment. For certain kinds of ware, pigments known as underglaze colours are applied before glazing, and these are more nearly related to the engobes than the glazes.

Apart from the increased resistance to external influences, imparted to the ware by glaze, by the vitreous nature of the latter, the application of glazes and engobes is chiefly for

artistic purposes, with the object of imparting lustre, smoothness, and colour to the surface of the ware. In an æsthetic sense the maximum of possibility has now been achieved, since there is no known degree of lustre or shade of colour that cannot be reproduced on ceramic ware; and, by means of suitable engobes, it is possible to produce the finest colouring on pieces made of ordinary ugly clay. This is a circumstance of special importance in many cases, where the problem of imparting a superficial imitation of fine ware to articles of inferior character, such as stove tiles, and facing bricks or tiles for building purposes, is in question. In this connection, also, a very high degree of perfection has now been attained, and the potter's handicraft raised to the dignity of a fine art in this branch too.

CHAPTER II.

GLAZES AND THEIR COMPOSITION.

ACCORDING to their composition, glazes may be classified into three chief groups :

1. Salt glazes ;
2. Earthy glazes ; and,
3. Fused or fritted glazes.

The first group, salt glazes, may be dismissed in a few words, their production requiring no special study or preparation. They are applied while the ware is in the kiln, by throwing a certain quantity of common salt into the kiln at a certain stage of the baking process.

The reaction produced is as follows:—The common salt (sodium chloride) is vaporised, and decomposes on coming into contact with the water vapour present in the furnace gases, to form sodium oxide and hydrochloric acid. The oxide combines with the silicates of which the earthenware consists to form a double silicate, a refractory glass, constituting a very thin layer firmly adhering to the substratum and forming a coating that is only slightly attacked by the strongest chemicals, glass being one of the most resistant substances known. Salt glaze is applied to the majority of stoneware articles, especially such as are used in factories where chemical products are made.

The second group, or earth glazes, consist of bodies insoluble in water. The chief point in their preparation is to mix the ingredients as intimately as possible, and bring

them into an extremely fine state of division. This is effected by grinding the mixtures to an exceedingly fine powder.

The fritted or fused glazes forming the third group are really the most perfect of all, and are prepared in a merely fritted or sintered mass, or as a completely fused mass of vitreous character. Owing to the high uniformity obtainable by fusion, this operation is sometimes applied to the earthy glazes as well, so that there is no sharp line of demarcation between these two classes. Fusion, however, is an essential feature of the fused glazes, because some of the ingredients are soluble in water and therefore cannot be ground wet. They also present so many other advantages over the earthy glazes that the latter are being more and more displaced, even for cheap ware. True, the fusing of the glazes, in the first place, increases their cost, but this is more than outweighed by the greater convenience in application.

It is clear that when earthy glazes are used, the actual glaze is not formed until the ware is baked, and in these circumstances it is easy for bubbles to be formed which greatly impair the appearance of the pieces. Hence, in order to obtain uniform glazing, it is essential that the ingredients of the glaze should be ground as finely as possible and mixed together so intimately that a uniform coating is produced when the ware is fired.

When, as is frequently the case with earthy glazes, a lead compound is present in the mixture, it may happen that the heavy lead compound settles down out of the mixture, owing to its higher specific gravity, in which case the glaze will be of irregular character.

This is one of the reasons why earthy glazes are going out of use, except for very common articles, and for the same reason even common glazes are now generally fused, this operation yielding a uniform mass which does not need

to be so finely ground as the earthy glazes, though it will give a perfectly even coating, free from bubbles, when fired.

Owing to the difficulty, on the one hand, of avoiding the use of lead in glazes for common ware, and on the other to the poisonous character of the soluble lead compounds, care must be taken that the lead compounds are contained in such a form in the glaze that they are not easily attacked by acid foods. The only way to ensure this result is to endeavour to obtain a lead-alkali silicate that contains sufficient silica to withstand the action of acids. Since, in the case of cooking utensils, acetic acid is the most usual form of acid encountered, the hygienic regulations of various countries now prohibit the use of lead glazes that are attacked by 4 per cent. acetic acid when boiled with the same for half an hour.

In compounding glazes care must be taken that the glaze has a lower fusing point than the ware to which it is to be applied. This condition is easily fulfilled, since even common clay has a fairly high fusing point; but if the two fusing points were very close together, the pieces would inevitably be distorted in the glost kiln. The same applies to engobes, which must have a higher fusing point than the glaze, and be fired at a temperature just sufficient to cause them to adhere firmly to the ware, without melting. Engobed ware is therefore always dull when fired, and only acquires its lustre by subsequent glazing.

The fusing-point of the glaze is a most important factor for the success of the glazing, and is correct when the fired glaze melts to a liquid which distributes evenly over the entire surface of the piece and forms a vitreous coating when cold. If the glaze be too refractory, the finished ware will be dull in patches, showing where the glaze has been unable to flow properly. Conversely, glaze that is too fusible will appear thick in some places, and thin in others.

FUSING POINT OF GLAZES.

The fusing point of a glaze depends on the nature of the ingredients used, just as much as on the relative quantities employed. The glazes are glasses, the acid constituent of which is usually silica exclusively, more rarely accompanied by boric acid, the acid or acids being combined with basic substances to form silicates or boro-silicates. In these compounds the fusing point of the glazes is determined—

1. By the equivalent proportion between acids and bases ;
2. By the proportion of alumina in relation to the bases and acids ;
3. By the ratio between the silica and boric acid.

The richer a glaze is in silica the less readily does it fuse, and therefore the modification of the proportion of silica in a glaze affords an excellent means of regulating its fusibility. Conversely, when a glaze contains too little silica, it is generally too fusible, and then either sinks into the porous substratum, or runs off the surface of the ware. An excessive silica content, on the other hand, results in the glaze either not fusing uniformly or else decomposing and becoming “devitrified” and dull, on prolonged exposure to the firing heat.

The bases present in the glaze have also a certain influence on the physical character of the product, a considerable analogy existing in this respect between them and the components of glass metal. Most of the ordinary kinds of glass consist of calcium silicate in combination with potassium or sodium silicate. A glaze containing only one or other of these alkali silicates together with the calcium silicate is always more infusible than one in which, whilst retaining the same relative proportion between the silica and the basic constituents, both potassium and sodium silicate are present with the calcium silicate.

Glazes containing considerable amounts of alumina can only

be used when the glaze material is fused at a very high temperature, since it is only under these conditions that alumina forms fusible compounds with silica. In such cases, therefore, alumina can be employed to make the glaze more refractory and check its tendency to run.

Just as in silica and alumina we have means available for raising the fusing point of glazes, so also in boric acid we have a means of reducing that fusing point. It may be remarked here, that silica and boric acid are mutually replaceable; consequently, when a portion of silica is replaced by boric acid, this must be done in such a manner that the total amount of acid remains unaltered.

From the foregoing remarks a series of prescriptions can be laid down for correcting the fusing point of a glaze.

The fusing point of a glaze is raised—

1. By increasing the proportion of silica in the mixture, without changing that of the bases;
2. By replacing a portion of the boric acid by silica, in the case of glazes containing both these substances;
3. In glazes containing lead oxide, by replacing a certain part of the lead oxide by equivalent quantities of potash, soda, lime or magnesia, leaving the other constituents unchanged;
4. By replacing potash-soda by potash or soda alone, or taking lime or magnesia alone in place of lime-magnesia, without altering the acid content;
5. By introducing alumina into the composition, when the glaze is intended to fuse at a high temperature only.

When a too refractory glaze is to have its fusing point lowered, the precisely opposite course must be pursued in each case.

THE CONSTITUTION OF DEFECTIVE GLAZES.

Sometimes it happens that glazed ware preserves its original fine appearance for a considerable time, but afterwards alters

in such a way as to clearly indicate defective constitution. To guard against the very unpleasant consequences that may ensue from sending out large quantities of such defective ware, it is essential to subject the glaze, or glazed test objects, to a series of tests, which they must pass before the glaze can be regarded as properly compounded. These tests will be described later on.

A glaze is properly compounded when it will stand considerable fluctuations of temperature without undergoing alteration. A glazed piece of earthenware, *e.g.* a pot glazed inside and out, consists of three strata: the two external thinner layers being composed of glaze, whilst the third and thicker one is the body or shard of clay. It is essential that, when the vessel is exposed to a heightened temperature, the glaze and body should exhibit exactly the same coefficient of expansion, so that in proportion as the shard expands, the glaze will follow suit, the two contracting equally on re-cooling, and the appearance of the vessel consequently remaining unaltered.

If the glaze, however, possesses a different coefficient of expansion from that of the body of the ware, then, as the temperature changes, a strain will be set up between the two substances, which strain may proceed so far as to overcome their mutual cohesion, and either loosen or separate them entirely.

In addition to these purely physical evils, others may arise that originate in the chemical composition of the glaze. We will deal first with the physical alterations, which manifest themselves by the following phenomena:—

The glaze cracks (“crazes”) all over, the surface exhibiting a complete network of lines as fine as a hair, some portions becoming detached and falling away, probably carrying with them small fragments of the body of the ware. In extreme cases the untouched pieces have been known to burst with a

considerable report into a number of pieces, scattered to a distance—probably in consequence of a slight change in temperature. In many cases the glaze is found to be cracked only at the edges, but these cracks will gradually extend over the whole surface.

When the coefficient of expansion of the glaze is higher than that of the body of the ware, it will expand more rapidly than the latter on heating; and since the latter, on account of its greater thickness and the low heat-conducting properties of the clay, cools more slowly than the glaze, this in turn contracts the more rapidly of the two, with the result that its cohesion is destroyed, and it breaks into a number of innumerable small fragments, bounded by hair cracks. The latter eventually get filled with dust and show up more and more clearly as dark coloured lines.

These cracks are frequently observed on old Chinese porcelain, the pieces then being classed as "*vieux craquelé*." At one time this class of ware had a certain vogue among collectors, and numerous imitations were produced; as a matter of fact, the frequent appearance of crazing on old Chinese ware is merely a proof that the old makers used glazes of defective composition.

When the conditions are such that the coefficient of expansion of the body of the ware is greater than that of the glaze, the latter will tear at the edges, or spring off in parts; and in extreme cases the whole piece bursts with violence.

Apart from the foregoing defects, arising from unequal coefficients of expansion, there are others which are attributable to the chemical character of the glaze.

When the materials used are not chemically pure, the mass contains impurities, some of which, like the sulphates and chlorine compounds, may be a source of considerable difficulty. At a very high temperature, the sulphates are decomposed by silica, though not at the temperature of the glost kiln; and

the chlorides are decomposed by considerable heat, but only when water vapour is present.

In presence of a very small quantity of sulphates, the glaze becomes coated with a misty film, which reappears when wiped off; and when the proportion of sulphates is large, the glaze is dull and void of lustre, or exhibits a number of wrinkles and bubbles. These latter are formed in consequence of the partial transformation of the sulphates into acid salts, which at higher temperatures part with the surplus sulphur trioxide, and this blows out the soft glaze in the form of tenuous bubbles. On the surface being wiped over with a cloth, these very thin bubbles are broken, leaving the surface rough to the touch. Dust gradually accumulates in the cavities, and forms dark specks. Defective glaze of this kind is sometimes known as "measly."

The so-called drying of the glaze on the edges of plates is due to the presence of sulphates in the glaze. The liquid portion of the glaze is less readily absorbed at the thin edges, and the soluble sulphates migrate to these parts, and finally crystallise there. When the glaze is fired, the edges become covered with dull patches and bubbles.

This effect of sulphates may appear remarkable, because a sulphate, *i.e.* gypsum, is largely used in the preparation of many porcelain glazes. It should, however, be remembered that the porcelain kiln frequently contains a reducing atmosphere, which decomposes the calcium sulphate, liberating the volatile sulphur dioxide, whilst the lime enters into combination with silica.

In the event of glazed ware exhibiting any of the aforesaid peculiarities, the maker must chiefly endeavour to prevent their recurrence, since otherwise his output would consist almost entirely of "wasters." Two ways are open: either by modifying the composition of the body so that it will have the same coefficient of expansion as the glaze, or else by

adapting the composition of the glaze to the character of the body.

In the former case the composition of the body can be modified only when the latter is compounded of several substances, as happens with all fine earthenware. This is out of the question with inferior ware, since in this case the usual practice is to merely prepare the available clay in a suitable manner so that it will furnish a plastic mass; and in these circumstances a remedy must be sought by modifying the composition of the glaze in order to make its coefficient of expansion agree with that of the body.

In connection with modifying the composition of the body, certain general rules can be established. When the glaze is found to craze, a trial can be made on the following lines:—

The proportion of clay in the body is reduced and the amount of silica concurrently increased. If China clay be used, a portion of this may be replaced by a highly plastic clay. In the case of bodies containing felspar, the proportion of this substance should be diminished, or else the silica present should be more finely ground than before.

Sometimes—though rarely—crazing can be prevented by firing the unglazed ware at a higher temperature.

When the defect shows itself in the form of cracked edges or partial peeling, the reverse procedure should be adopted.

When the composition of the glaze is to be altered to effect a remedy, leaving the body unchanged, the following method is recommended, provided the defect manifests itself in the form of crazing.

The proportion of silica in the glaze is increased, thus raising the fusing point.

All the ingredients of the glaze are left in their original proportions, except the boric acid which is increased, with the result that a somewhat lower temperature can be employed in the glost kiln.

Should the defect consist in cracked edges or peeling of the glaze in places, the converse procedure must be followed.

It may happen that despite the composition of the body and glaze being mutually suitable, no handsome, uniform glaze is obtained. In such event the most important point is to see that the body is perfectly homogeneous, since, when the body contains large internal cavities, it will never glaze evenly, the irregular thickness of the body causing unequal absorption of the glaze.

When porous shards are dipped in glaze, the air-bubbles imprisoned in the body of the former are expelled and dislodge the glaze, so that when the piece is fired the glaze will have a pock-marked appearance. When the piece to be glazed has already been fired—which will generally be the case with finer ware—it must have been baked thoroughly, or else the glaze will always turn out uneven, crazing while in the kiln and running together in places to form drops, which then appear as warty excrescences.

The glazing of previously unbaked ware is attended with certain difficulties, and is only successful when the pieces have been dried till they are as hard as leather, and the glaze is used in a viscous state. The pieces do not then get damp in the dipping process, the time being too short to allow any absorption of water to occur; they come out of the glaze tub in a wet state, but soon dry, part of the water being absorbed, the rest evaporated. Pieces treated in this manner must not be fired until thoroughly dry.

The pulverulent particles of glaze will not adhere firmly to the surface of the ware—no matter whether the latter be merely air-dry or fired—unless the articles are perfectly free from dust. Every speck of dust lying on the ware forms a stratum separating the latter from the glaze; in the firing process the organic matter of the dust particles is destroyed, to the invariable accompaniment of a liberation of gas or

vapour; and, however slight this may be, it is sufficient to produce an irregularity in the glaze, a dark grey patch, a dull spot or a bubble.

THE PRACTICAL TESTING OF GLAZES.

When one has to work with a glaze of different composition to that hitherto employed in the works, it is essential to first make a trial with it on a small scale, to preclude the possibility of spoiling a whole batch of ware. For this purpose a small quantity of the glaze is prepared, taking care, however, to weigh out the ingredients exactly according to the formula given. Owing to the small quantities employed for these tests, several different glazes can be tested together.

If one recipe gives a glaze that is too refractory, the next one with a somewhat lower fusing point, and so on, a few trials will suffice to furnish a mixture giving perfectly satisfactory results. Small defects revealed in the trials can be easily rectified in mixing the glaze mass in bulk.

The two chief factors concerned relate to the fusibility of the mass and to the behaviour of the glaze when fired (whether the glaze crazes, tears at the edges, cracks off, etc.).

It is important that the ceramist should know the approximate temperature at which his glazes fuse, and for this reason appliances are used which indicate the fusing point exactly.

For this purpose it is highly convenient to make use of certain metals, the fusing points of which have been definitely ascertained, so that the limit of possible error in the fusing point will not exceed about 20° C. These metals and their fusing points are given below—

Zinc	fuses at 412° C.
Aluminium	700° "
Silver	between 954° and 986°	" "
Gold	" 1045°	" 1093° "
Copper	" 1054°	" 1097° "

Nickel . . .	between 1476° and 1715° C.
Palladium . . .	1500° „ 1643° „
Platinum . . .	1757° „ 1855° „

These fusing points, however, cannot be relied on unless the metals are perfectly pure. The form in which the metals are used is that of a very thin foil, cut into triangles measuring about 2 mm. along the base and 5 mm. high.

These trial strips are placed, for use, on a porcelain plate covered with a layer of calcined magnesia about 5 mm ($\frac{1}{5}$ th inch) deep. Several small cavities are made in the powdered magnesia with a rounded tool, and in these depressions the strips of metal are laid. The whole is then placed in the apparatus in which the glaze is to be fired; and the moment the glaze fuses, the plate is withdrawn from the apparatus. The metal strips that have fused into small globules will give the fusing temperature of the glaze; and if one of the strips has just begun to melt at the tip, this will imply that the temperature in the furnace had already nearly attained the fusing point of that particular metal.

For the fusibility test the glazes are made up into small cones 20 mm. high and 10 mm. across the base, by mixing the glaze powder with sufficient thin gum water to make a plastic mass. This mass is pressed into a divided hollow metal mould, which is then taken apart, and the cone removed and dried slowly.

A number of these cones are placed on a plate made of the same body as that of the ware on which the glaze is to be used; and a number of other cones, coated with a little gum water on the base, are placed on a second plate of the same size. The first plate is laid horizontally in the furnace, the second being inclined so that the fusing cones may run down in narrow streaks over the surface.

After firing, the cones are examined, whereupon it will be found that the most refractory will have merely collapsed or

sintered, whilst the more fusible ones will have melted to a circular disc on the horizontal plate, the centre of the disc being thicker than the edges.

On the inclined plate the least fusible cones will have retained their shape more or less completely; whilst the more fusible ones will have curled over at the tips. The length and breadth of the streak formed by the flowing mass will also afford indications of its behaviour in firing.

Another test performed at the same time as that with the cones is by applying the glaze, by dipping, to the surface of plates 4 in. square, and therefore having an area of 16 sq. in. The behaviour of the cone gives the fusibility of the glaze, and that of the glazed plates shows whether it has any tendency to craze or exhibit other defects.

With this object the plates are subjected to repeated rapid fluctuations of temperature, by immersing them in boiling water until they can be assumed to have acquired that temperature, whereupon they are plunged into cold water. The glaze should not show any signs of alteration after repeated subjection to this test: it must not craze, tear at the edges, or spring off. In the case of ware intended to stand even higher temperatures—chemical apparatus such as crucibles, basins, and the like—the test must be more severe. Glaze for this kind of vessels must be rapidly heated to redness and quickly cooled in the air, and stand this test without alteration. It should be remarked that the glaze for these articles is applied very thin, in order to enable the body and glaze to expand and contract together more uniformly.

In testing glaze for earthenware cooking utensils, it is important that the mass should be of such a nature that it is not corroded by acids, and is free from poisonous metals, lead in particular, that might find their way into the food. These glazes are tested by dipping the glazed test plates in

a glass or porcelain vessel charged with vinegar containing not less than 4 per cent. of acetic acid, and boiling them therein for half an hour. The glaze should emerge from this treatment unchanged, and not have ceded any soluble metallic compounds to the vinegar.

Glazed earthenware has latterly come into vogue for decorative purposes in building. Such ware must therefore be able to stand the influence of weather, changes of temperature, and the action of air and water. Glazes which will pass the foregoing tests may be considered capable of retaining their appearance out of doors. The chief point, however, is resistance to the air.

The air, as is well known, contains certain minute quantities of carbon dioxide (carbonic acid) and ammonia, which substances, in conjunction with water, act on glaze, and in course of time spoil its appearance, the lustre being chiefly affected.

Glazes that are not weatherproof exhibit the same phenomena as can be seen in the case of imperfectly compounded glass, *i.e.* losing their lustre when exposed to air containing carbon dioxide and ammonia (the windows of cow-houses, for example), becoming coated with a whitish film, and finally iridescent and opaque. The action of the carbon dioxide and ammonia decomposes the superficial portion of the glass and produces devitrification.

The same kind of thing is observed with glazed articles exposed to the air. Since, however, it may be some years before the gloss is weakened and iridescence appears with a glaze that is of comparatively good composition, it is advisable to employ a test which will reveal this tendency in a very short time if it exist at all.

For this purpose a porcelain basin containing concentrated hydrochloric acid is set on a plate of porcelain, and above this basin are placed the plates with the glaze to be tested—glazed side up,—the whole being covered with a bell glass.

The hydrochloric acid vapours liberated from the basin act powerfully on the glaze, and unless the latter possesses high powers of resistance, it will become dull, as though breathed on, within a few days. Iridescence makes its appearance later, but soon vanishes, leaving the surface dull once more. On bringing the plate into the air, the surface of the glaze will be found covered with a very delicate white dust, consisting of silica deposited by the decomposition of the glaze. When glazes fail to stand this test, they cannot be considered weatherproof, as, after exposure to the outside air for a few years, they would suffer the same changes as those set up by the action of hydrochloric acid for a brief period.

CHAPTER III.

GLAZE MATERIALS.

IT has already been mentioned that, from the point of view of their chemical composition, glazes must be classed as glasses. The only difference between them and ordinary glasses is, that their coefficient of expansion must accommodate itself as closely as possible to that of the ware on which they are to be fired.

Chemically speaking, all glasses are double silicates, *i.e.* they contain, in addition to silica, at least two metallic oxides, one of which corresponds to the formula RO , whilst the other is an oxide of the composition R_2O_3 . Hence the following may be regarded as a typical formula for glazes:—



The values of x , y , and z correspond to the number of equivalents of the several oxides present in the compounds.

The constituents of glaze may be classified to a certain extent by dividing them into glaze-forming and glaze-colouring matters. The former category comprises the substances forming perfectly colourless masses. The second or colouring substances are only present in small quantity, and serve the purpose of imparting a certain colour to the mass. Most of the glaze-colouring matters may be regarded as in a state of solution in the fused silicates, and as also taking part in the silicate combination. Certain of the pigmentary constituents do not dissolve in the glaze mass, but remain disseminated in a very finely divided state, in about the same way as a powder insoluble in water may be held in suspension therein.

The basic constituent representing the formula RO may consist of—potash, soda, lime, magnesia, lead oxide, and sometimes baryta ; whilst of the oxides having the composition R_2O_3 , alumina is the only one coming under consideration in the preparation of colourless glazes. Silica, which may occasionally be replaced by a certain quantity of borax, is used either in the form of pure quartz sand or ground quartz, or is employed in the state of a natural silicate, such as white clay or felspar.

The pigmentary oxides include the oxides of several of the heavy metals, principally iron, manganese, nickel, cobalt, and copper. These oxides are completely soluble in the fused colourless glaze, and impart thereto certain characteristic colours which can be shaded in various ways by using two oxides of different colours. Tin oxide, antimony oxide, and chromic oxide, which are also used as colouring constituents of glaze, do not dissolve, but remain in suspension in a very finely divided state.

Whereas, for the sake of securing purity of colour, the pigmentary oxides must be used in a very pure state, the materials for the colourless glaze must be employed in the form in which they are met with in commerce, and therefore perfect purity cannot be counted upon. It may be remarked here that it is unnecessary that potash, for example, should consist of pure potassium carbonate, a sample containing only 90 per cent. of the pure salt being quite suitable. It must, however, be free from any metals capable of colouring the glaze, the production of a perfectly colourless glaze being otherwise impossible.

The same naturally applies to all the other ingredients used for making colourless glazes. When a sufficiently pure raw material is unobtainable, there is no other course open than to subject it to a special treatment in order to eliminate the colouring substances. Iron compounds being so very wide-

spread in nature and capable, when present even in minute quantities, of imparting a yellow tinge to glaze, these are the substances chiefly to be borne in mind as necessary to eliminate from the raw materials before the latter can be used for making colourless glazes.

The silica for glazes is most frequently used, as already mentioned, in the form of quartz sand or powdered quartz. The great hardness of this substance makes its reduction to powder a matter of great difficulty, but the operation may be facilitated by heating the fragments of quartz to redness and then throwing them into cold water, the rapid cooling rendering the quartz extremely brittle, and consequently easy to convert into powder.

However, before quartz or sand is used for making glaze it must be tested for the presence of iron. With this object a small quantity of the powder is extracted by boiling with hydrochloric acid, and the liquid is tested for ferric oxide. If the latter be found and no iron-free quartz is obtainable, there is no alternative but to perform the operation known in the trade as "bleaching." This consists in treating the finely powdered quartz in a vat with a mixture of 1 volume of concentrated hydrochloric acid and 9 volumes of water, leaving them in contact for several weeks. The iron oxide dissolves in the hydrochloric acid, and after drawing off the solution, the residual quartz is freed from acid by washing with water.

Even with this treatment, however, it is impossible to extract the whole of the iron, and glazes made with such quartz are never perfectly white, but always exhibit a yellow tinge when viewed on a white background. Nevertheless, they may be made to appear perfectly white by an artifice that is of great value in the manufacture of glazes.

Ferric oxide colours the glaze yellow, whilst cobalt oxide imparts a blue tinge, so that by treating a yellow-tinted glaze with a corresponding quantity of cobalt oxide, a colourless glaze

is obtained, the two colours, blue and yellow, being complementary and producing white when mixed in the right proportions.

Silica is also used in the form of minerals, very often in the state of white clay (aluminium silicate) or felspar (potassium (sodium)—aluminium silicate). Since the presence of iron in these minerals also would preclude the formation of a colourless glaze, they must be freed from iron before use.

Boric acid can be used in partial substitution of silica, since it forms with lime, magnesia and lead oxide, insoluble vitreous compounds that are, however, more fusible than the silicates. The sodium salt, borax, may be used instead of the pure acid, but as it contains a considerable amount of water, it must be dehydrated and fused by strongly heating it before use as a constituent of glaze. The anhydrous borax then appears as a hard, colourless mass of vitreous appearance.

Potash is used in the form of potassium carbonate, or as nitrate (saltpetre), which latter is readily obtainable free from iron, whereas the carbonate may contain iron and manganese oxides, capable of producing colour, and must therefore be tested for these impurities before use. Manganese oxide imparts a bluish tinge to the glaze, but this can be compensated, when present, by the addition of a very small quantity of ferric oxide.

Soda may be used in various forms as an ingredient of glazes. The carbonate is most frequently employed, preferably in the form known as "enamel soda," which is distinguished by its entire freedom from iron compounds. For glazes in which a portion of the silica is replaced by boric acid, ordinary borax may be employed as the source of soda. Sodium chloride (common salt) may also be employed, but sodium nitrate is rarely used.

Lime is employed in the form of non-ferruginous limestone, *e.g.* various kinds of marble, dense limestone, or chalk.

Magnesia is used exclusively in the form of the mineral magnesite.

Barytes come into use in two forms: the mineral witherite (barium carbonate), and heavy spar (barium sulphate).

Lead oxide, which is of special importance in making glazes, may be derived from several sources. For common glazes, native galena (lead sulphide) is often used; but for finer qualities preference is given to litharge, red lead or white lead (carbonate). The latter being obtainable in a very pure state in commerce, is used almost exclusively for the finest glazes.

Apart from the foregoing chemical products, a number of minerals are used in practice as glaze-forming materials, chief among them being the following. Preference is generally given to minerals that can be obtained of uniform character in all cases.

Kaolin or porcelain earth is a mineral with the composition, Al_2O_3 , 2SiO_2 , $2\text{H}_2\text{O}$, and therefore always introduces the two constituents, silica and alumina, simultaneously into the glaze, a fact that must be remembered in compounding glazes.

Felspar is an important mineral in the preparation of many glazes. A large number of varieties of this mineral are known, and the composition of the one in use must therefore be ascertained, in order that the glaze may have the desired properties. There are two chief kinds of felspar: potash felspar and soda felspar, the former having the composition, K_2O , Al_2O_3 , 6SiO_2 , whilst in the latter a larger or smaller proportion of the potassium is replaced by sodium. In virtue of their composition, these minerals introduce silica, alumina, and potash or soda (sometimes both) into the glaze.

Borocalcite, sodium-borocalcite are minerals used in making glazes, the former consisting of lime and boric acid, the latter of lime, soda, and boric acid.

For many glazes, both fine and common, use is also made of ground shards that have been thrown out as wasters and unfit

for sale. Porcelain meal is often used as an adjunct to the finest glazes; stoneware meal for second qualities, and brick-dust for common coloured grades. Apart from adding to the quantity, these substances are chiefly used to reduce the shrinkage of the glaze on the ware.

If the pigmentary metallic oxides be added to the list of glaze constituents, the range of materials collaborating in the formation of glazes becomes a very wide one.

Hence, in order to obtain properly constituted glazes for any given ceramic ware, the glaze manufacturer must carry on a series of exhaustive investigations and experiments in the laboratory. No invariable rules can be laid down in this case, the character of the clay being different in each pottery, so that a glaze which gives excellent results in one case will turn out quite useless in another.

Of course, any glaze can be imitated; but the requisite method is troublesome and tedious. The first step is to subject the pattern glaze to an exact quantitative analysis, the results of which will furnish a guide to the relative proportions of silica and oxides of the composition RO and R_2O_3 . The composition of the available minerals being known, the corresponding quantities of the individual constituents can be calculated so as to furnish a product of the same composition as the pattern.

It will next have to be ascertained by experiment, whether this glaze is suitable to the ware to which it is to be applied, since the firing test may reveal the defects to which reference has already been made. In such event, the composition of the glaze must be altered accordingly, so that, eventually, a glaze suitable to the conditions prevailing in the works may be produced.

The foregoing operations are so tedious that they would occupy a chemist for a very considerable time, and they are therefore seldom carried out in practice, the usual plan being to make

practical experiments from the outset, utilising at the same time the data furnished by analytical chemistry as to the composition of glazes of different properties. In this connection, schemes have been drawn up, on the basis of numerous analyses, whereby a favourable result may be reliably expected after a few trials. These schemes, as established for various glazes, are given below, the quantities indicated in all cases referring to equivalents or multiples or fractions of equivalents.

Felspar and kaolin being very often used in making glazes, it is important to bear their composition in mind when calculating formulæ. The general composition of felspar is represented by the symbol K_2O , Al_2O_3 , $6SiO_2$, whilst pure kaolin has the formula: Al_2O_3 , $2SiO_2$, $2H_2O$.

The glazes used for the different kinds of earthenware differ in composition just as widely as the body of the ware. Whilst readily fusible glazes of relatively low hardness and resistance to chemical agencies will do for ordinary pottery, the glazes for the finer grades (porcelain) must have a very high fusing point, extreme hardness, and a power of resistance to chemicals that is possessed only by the very best glazes.

Between these two extremes of the ceramic scale, common pottery and porcelain, are a number of intermediate stages, such as faience, stoneware, etc., of various qualities. The finer the ware, the finer, *i.e.* more refractory and resistant, must be the glaze, this body determining the appearance and value of the whole article.

In the subjoined formulæ, RO expresses either potash, soda, lime, magnesia, lead oxide, or baryta. Al_2O_3 is the alumina, and can, in the case of coloured glazes, be partly replaced by the similarly constituted ferric oxide (Fe_2O_3), manganese oxide (Mn_2O_3), or chromic oxide (Cr_2O_3). Similarly, a portion of the silica (SiO_2) can be replaced by boric acid, either in the free state or in combination as borax.

COMPOSITION OF GLAZES FOR ORDINARY POTTERY.

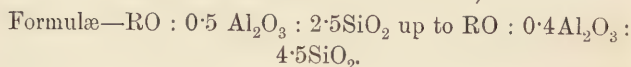
(Utensils up to Faience of Good Quality.)

For this purpose, the most readily fusible glazes are used, generally rich in lead oxide, the limits of the formulæ being—



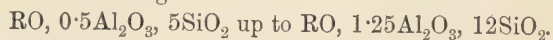
COMPOSITION OF GLAZES FOR HARDER WARE.

(English and German Stoneware.)



COMPOSITION OF GLAZES FOR PORCELAIN.

These are the hardest and most refractory of all, the limits of the formulæ being—



Note.—The substances, such as tin oxide, etc., that are used solely for rendering glazes opaque, are not mentioned in the above formulæ, since they do not play any part in the chemical composition of the mass, but are merely incorporated therewith in a finely divided state in order to render the same opaque, or colour it white.

CHAPTER IV.

THE PREPARATION OF GLAZES.

OBSERVATION having shown that even low grade pottery acquires an improved appearance when coated with a uniform, lustrous glaze, the primitive methods formerly used in preparing ordinary glazes have gradually been abandoned in favour of those calculated to furnish a uniform product, which will give a perfect and even coating when fired on the ware.

The operations to be performed in preparing glazes on a manufacturing scale are generally as follows:—

1. Testing the purity of the raw materials employed.
2. Converting these materials into fine meal.
3. Mixing the various ingredients in the suitable proportions.
4. Fusing the mass.
5. Grinding the fused product.

The first point may be omitted, in the case of low class glazes, as of little importance. Most of these glazes are coloured, and it really does not matter if the sand, for instance, contains so much ferric oxide that a yellow to reddish-brown colour is imparted to the glaze. The case is, however, different when dealing with glazes intended for finer ware, the complete absence of colour being then essential, whether the glaze is to be used in that state or designedly coloured. In the latter event the presence of a ferric oxide coloration in the glaze would seriously affect the beauty of the colour in most instances.

TESTING THE PURITY OF THE RAW MATERIALS.

It has already been mentioned, more than once, that iron compounds are so widespread in nature that this metal, especially in the form of ferric oxide, is found in nearly all the mineral substances used in the production of glazes. Owing to the yellow tinge imparted to glaze by this oxide, even when present in minute quantities, it must be eliminated in the preparation of all glazes used for fine ware.

The method of removing iron from ferruginous sand by boiling it with hydrochloric acid has already been detailed; and also the fact that the colour produced by very minute quantities of iron oxide can be masked by adding a certain proportion of cobalt oxide to the glaze, the amount taken being large enough to compensate the yellow ferric oxide stain by the blue colour set up by the cobalt oxide, thus making the glaze appear colourless.

When lime is used in the glaze, it must be carefully examined for the presence of iron, highly ferruginous lime being entirely unsuitable for fine glazes. In such cases, however, the lime contained in white marble is advisable; and the white marble cuttings or chippings from sculptors' studios can be advantageously utilised for this purpose.

The potassium and sodium salts are very important constituents of fine glazes. At present it is easy to obtain potash that is almost entirely free from iron, or failing this, use can be made of potassium nitrate, which occurs in commerce perfectly pure in this respect. The sodium compound most frequently used by glaze manufacturers is the carbonate, which is now also obtainable perfectly free from iron.

If white marble chippings are not available, the best source of non-ferruginous lime is chalk, which consists of the calcareous envelopes of microscopic marine animals, and is perfectly free from compounds of iron.

Lead oxide is also an important ingredient in many glazes, especially those desired to have a low fusing point. In the case of glazes for common ware, in which the colour of the glaze is immaterial, lead is often used in the form of the mineral galena (lead sulphide). For colourless glazes, however, artificial preparations of lead must always be employed, such as ordinary lead oxide or litharge, the peroxide (red lead), and finally white lead (carbonate).

Commercial litharge, when sufficiently pure, forms a very good material for lead glazes, but the majority of the commercial brands contain certain small quantities of pigmentary oxides which naturally affect the colour of the glaze. A very minute quantity of these oxides is sufficient to spoil litharge for the purpose in question; and, in fact, when the amount of the foreign metal exceeds the percentages given below, the litharge becomes quite unsuitable for use in colourless glazes:

Copper	0.0041 per cent.
Antimony	0.0050 „
Bismuth	0.0050 to 0.0075 „

These figures have been given for the special purpose of showing that even extremely small quantities of impurities can spoil the appearance of an otherwise perfectly suitable glaze.

Red lead is a product that can be advantageously used in most cases for the preparation of glazes. For this purpose it should be made from a litharge that contains no more than traces of iron or copper compounds, it being otherwise impossible to obtain a red lead of brilliant appearance and pure shade. Red lead also exerts a beneficial influence during the fusing of the glaze mass, inasmuch as it liberates a certain amount of oxygen during the process, which oxygen acts upon and eliminates any organic particles present in the form of dust, etc., and also converts any traces of ferrous oxide present—

which would introduce a green coloration into the less powerful yellow pigment, ferric oxide.

It should be mentioned that the presence of organic matter would, in the absence of free oxygen, greatly impair the appearance of the finished glaze. Without this free oxygen, the dust and other minute organic particles would merely carbonise during the fusing process, and form small black specks which would spoil the look of the glaze, a skilled eye immediately detecting the grey tinge of such glaze.

The dearest, but also the best, lead compound used for glazes is the carbonate, white lead, which contains scarcely a trace of extraneous metals, and in any case the quantity is so minute that it does not interfere with the usefulness of the carbonate.

Another lead salt excellently adapted for the purpose in view is lead sulphate, which can generally be obtained at a low price from chemical manufacturers, who find it difficult to dispose of. Being almost invariably chemically pure, from the method of its preparation, it is admirably adapted for the production of colourless glazes.

The substances mentioned above are those used in the manufacture of glaze, in the strict sense of the word. It will be evident, from what has already been said, that these glazes are really glasses, differing from one another in point of hardness, fusibility, and power of resisting chemical agencies. Their application also differs according to the value of the material from which the pottery ware is produced.

In many cases, however, the use of glaze is designed to mask the colour of the underlying clay, and thereby improve the appearance of the ware. This purpose is attained by mixing the colourless glazes with substances that either render them perfectly opaque, or at least milky and translucent. The substances added for this purpose do not enter into chemical combination in the glaze, but are merely embedded in a finely divided condition therein.

When these substances in suspension are themselves colourless, they make the bulk of the glaze either milky or quite white in appearance, according to the quantity employed.

Glazes may also be rendered opaque by substances which at the same time impart a certain colour to the mass. This may be effected in two ways: either by incorporating a sufficient quantity of pigmentary powder to effect this dual result, or else by making the glaze a coloured glass from the commencement. For instance, when the glaze has been so compounded that it forms a green glass, it will impart a certain tinge of green to the white body of the ware to which it is applied. On the other hand, when this green glass is mixed with a colourless substance which does not enter into chemical combination with the mass, a green colour will be obtained that is quite different from that produced by the transparent green glaze; and the shade can be varied to any extent by altering the proportion of the substance used for producing opacity.

Glazes may therefore be classified, according to their appearance, into three main groups:

1. Colourless glazes;
2. Opaque glazes of various colours; and
3. Transparent coloured glazes.

The substances employed in the preparation of these glazes are very numerous, and belong exclusively to the group of the heavy metals. At present we will refrain from more than mentioning these substances, leaving a description of their properties and application until we come to deal with the glaze masses in which they figure.

THE PREPARATION OF THE GLAZE MASS.

When glaze masses are to be made on a large scale, a certain series of operations must be gone through in all cases. The first of these consists in reducing the ingredients to the finest possible state of division; the second being to weigh out the

powdered ingredients accurately in the proportions they are to occupy in the mass, after which they must be mixed together, in such a manner as to ensure intimate admixture of the whole. This latter is a very important feature, since otherwise the mass would not be of uniform chemical composition throughout after the fusing process.

The preceding stages are mechanical operations, but the subsequent fusing process involves chemical reactions, namely, the formation of the silicates constituting the chief substance of the glaze. Formerly the preparation of ordinary glazes was confined to applying the powdered ingredients in the form of a pulp or dry powder to the surface of the ware and then fusing them on the latter, or else the ingredients were merely heated to a degree sufficient to form the silicates without causing the mass to fuse uniformly throughout, *i.e.* the glaze was merely fritted.

Neither of these methods producing the desired homogeneity of the glaze, they have now been abandoned, at least in the production of better class pottery, the general practice at present being to fuse the glaze completely before use.

The final stage in the production of glazes is again of a mechanical nature, for the purpose of converting the fused mass into a fine powder, which can afterwards be applied to the ware, either in the form of a milky liquid or in the dry state, and fused thereon in the kiln.

APPLIANCES FOR PULVERISING THE MATERIALS.

The mechanical devices used for powdering the materials for glaze must be adapted to suit the nature of the substances to be ground. The hardest of these substances are quartz and felspar; and though the former is often obtained in the state of sand, yet even the finest quartz sand consists of particles that are too coarse for the purpose in view, and therefore need further comminution. Moreover, solid quartz is often employed instead of sand for fine glazes,

consisting as it does of pure silica, which is rarely the case with sand.

The great hardness of quartz and felspar (which is not much softer) necessitates the use of crushing and grinding machinery capable of exerting a considerable amount of power. The other ingredients of glaze are comparatively soft, and therefore can be converted into powder by means of lighter machinery.

To facilitate the reduction of the quartz and felspar, these



FIG. 1.—Californian stamp mill.

substances are first heated to redness and thrown into water, which quenches or cools them suddenly, thereby producing brittleness and rendering the pulverising process much easier.

The machinery generally used for crushing consists of stamps or edge-runners. In the former the lumps of felspar or quartz are crushed by the impact of the falling stamps and delivered into screening devices which sort the product out according to the fineness of the particles.

A set of stamps of this kind is illustrated in Fig. 1, the

mill being of the type often used for crushing ore. Since, however, the iron or steel of which the stamps and trough are composed would undergo attrition and thus introduce the undesirable ingredient, iron, into the glaze material, it is necessary to face the stamps with quartz and line the trough with blocks of the same material.

Another type of machine for crushing hard materials is the edge-runner mill, illustrated in Fig. 2. In mills of this kind,

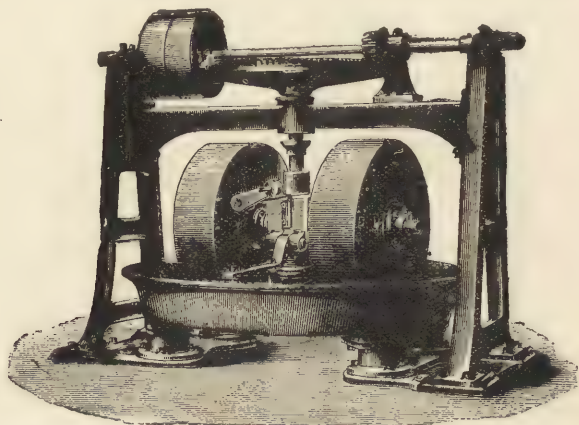


FIG. 2.—Edge-runner mill.

a vertical shaft carries a horizontal arm which passes through circular holes in a pair of mill-stones running in an annular trough. When the vertical shaft is set in motion, these stones run round inside the trough, like wheels, and crush the material placed therein by their weight. Hence, the heavier the stones, the greater the effect produced. Blades are provided for returning to the centre of the trough the larger fragments pushed aside by the runners.

In this case, again, to prevent the introduction of iron into the glazed materials, the working parts in contact with the

latter must be faced with quartz. With this object the trough is lined with quartz blocks, and the runners are either of quartz throughout, or of cast-iron with a rim of quartz blocks.

The crushed material is more finely powdered in other machines, chiefly ball mills or disintegrators. The former type of mill consists in principle of a drum surrounding a rotary horizontal shaft and containing a number of hard bodies or balls of bronze, steel, etc., though for glaze making these must

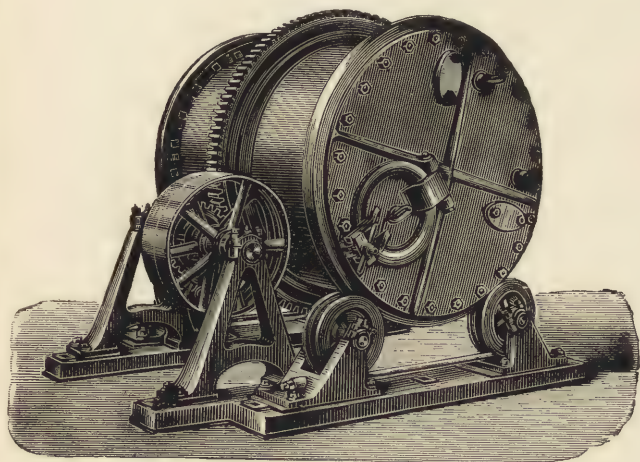


FIG. 3.—Ball mill, mounted on rollers.

be replaced by round quartz stones, and the drum lined with quartz, for the reason already advanced. As the drum revolves, the balls act on the material under treatment and reduce it eventually to a very soft powder. To prevent the finer portions impeding the action of the balls on the coarser particles, the drum is fitted with fine sieves through which the powder falls, or else a powerful current of air is forced through the drum, to blow the dust away into a collecting chamber.

When an extensive source of cheap motive power is available, *i.e.* water power, disintegrators can be advantageously employed for comminuting hard materials. These appliances chiefly consist of three or four open rings, the periphery being fitted with a number of sharp-edged steel prisms. The two innermost rings rotate in one direction, whilst the two outer ones turn in the opposite direction, at a high rate of speed

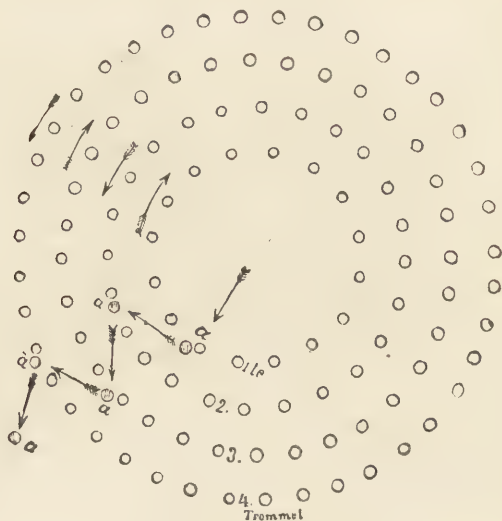


FIG. 4.—Arrangement of the rods in a disintegrator (Trommel=drum).

(Fig. 4). The material under treatment—marked *aa*—enters the mill inside the inner ring and is thrown by the centrifugal force with great violence against the sharp-edged steel rods. The resulting fragments are broken up still further by the rods of the second ring, and so on, until finally the powder is ejected from the mill. These disintegrators, one of which is shown open in Fig. 5, are also well adapted for mixing powdered substances, and can therefore be used for this dual

purpose in the preparation of glazes. Their disposition preventing any dissemination of dust, they are particularly suitable for mixing glazes containing lead compounds, it being very important to protect the workmen from the injurious effects of plumbiferous dust.

The softer materials for glaze can be ground in ordinary mills, either wet or dry (Fig. 6). When none of the materials is soluble in water, the wet method is preferable, this prevent

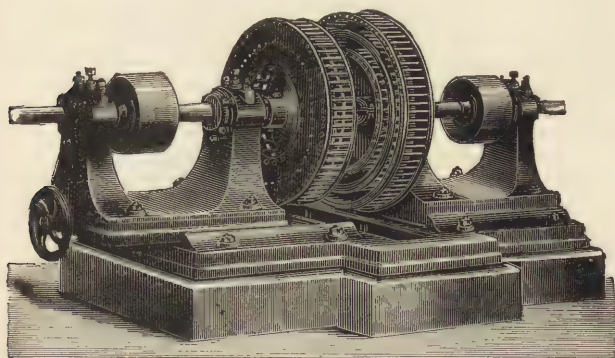


FIG. 5.—Disintegrator.

ing any formation of dust, and at the same time consuming less motive power than dry mills.

On the other hand, any ingredients that are soluble in water should be omitted from the wet grinding, and then added, in a dissolved state, to the ground mass, which then contains all the ingredients and can be put through the further stages of preparation.

When the glaze mass has been made into a pulp it must be worked up without much delay, or undesirable alterations will take place, especially if solid lead compounds, like red lead or white lead, be present, these specifically heavy bodies

settling down to the bottom, and causing irregularity in the composition of the fused glaze.

The pulpy mass can be quickly dried by spreading it out in shallow pans, heated by the flue gases from the melting furnace or other source of waste heat. If the mass be stirred up with

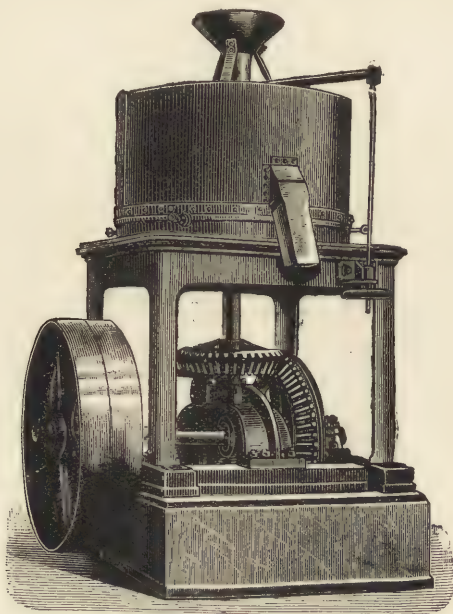


FIG. 6.—Mill with overhead running-stone.

a rake, the water is quickly expelled and the whole falls to a dry powder.

FUSING THE GLAZE MASS.

This operation must be performed in special appliances, arranged in accordance with the character of the material under treatment. Whereas glazes rich in lead have a relatively

low fusing-point, and can therefore be fused in a reverberatory furnace, the fusing-point of the other glazes is high, thus entailing the use of furnaces capable of generating very high temperatures.

Readily fusible glazes are often fused in a fritting furnace, as illustrated in Fig. 7, the shape being identical with that of a horizontal reverberatory furnace. The fire gases coming

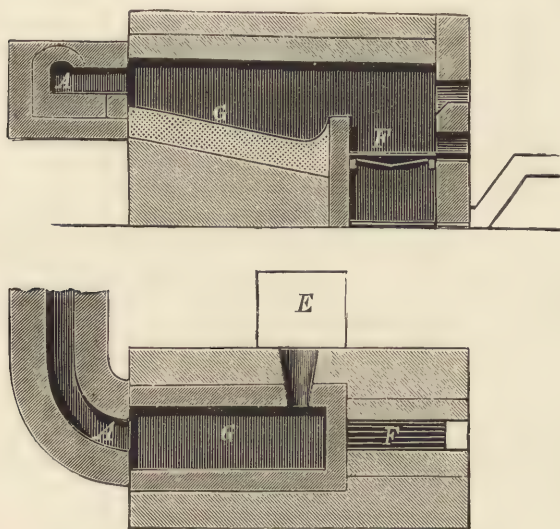


FIG. 7.

from the grate *F* pass over a firebridge and thence over a trough *G* with an inclined sole, on which the charge is placed and fused. The fused mass collects at the deepest part of the sole, and can be drawn off, through a tap hole *E* at the side, into a vessel of cold water, the sudden cooling causing the mass to set to a very brittle slag that is easily reduced to powder.

The charge to be fused is spread over the arch of the furnace while the preceding charge is being melted, so that it can be warmed up beforehand and lowered into the furnace as soon as the latter is empty. The usual dimensions of the furnace sole are 7-9 feet long and about 3 feet wide.

A modification of this type of furnace, for making glaze in larger quantities, consists in placing a layer of well-rammed

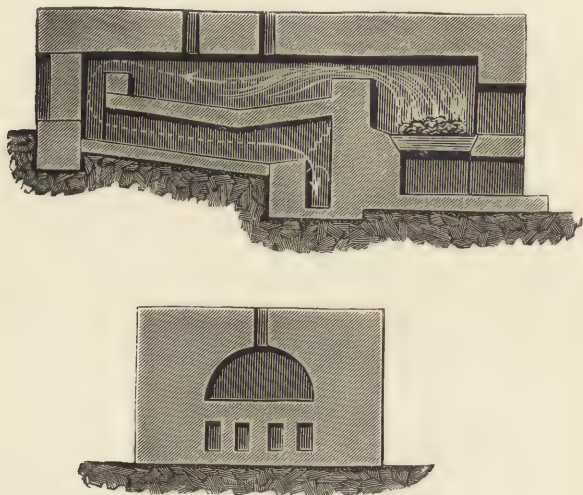


FIG. 8.

quartz sand in the lowest part of the sole and introducing the charge at the highest part. As soon as a certain quantity of the charge is melted, it flows down the sole and collects over the sand. A further portion of the charge is then introduced, and the operation is repeated until the deep portion of the sole is filled with the fused mass. The furnace is then left to cool until it is merely at a low red heat, whereupon water is poured on to the glaze mass which is thereby caused to break into

a number of fragments that can be taken out through a door at the side. In this manner a charge of up to 2 tons can be dealt with in a furnace of the foregoing dimensions.

These furnaces consume a large amount of fuel, the heat being applied over the surface of the mass only. It is therefore advisable to devise a means of leading the fire gases back underneath the sole before they pass away into the chimney.

Fig. 8 shows the arrangement of a similar furnace in which the sole has a double slope toward the middle. This type is very suitable for fusing mixtures of lead and tin oxides for making white glazes.

FURNACES FOR REFRACTORY GLAZES.

To fuse refractory glazes, the preceding types of furnace cannot be used, since the temperature developed is insufficient to liquefy the mass. In this case the operation must necessarily be performed in crucibles set in suitable reverberatory furnaces.

An older form of this class of furnace for refractory glazes is shown in Fig. 9. A fireclay cylinder, entirely open at the bottom and provided with an opening at the top, is mounted in an opening in the grate of a shaft furnace, where it serves as a support for a crucible containing the charge to be fused. The small hole—about $\frac{1}{8}$ th inch in diameter—in the bottom of the crucible, is closed with a porcelain ball before inserting the charge. When the crucible is surrounded with glowing coal, or preferably coke, the temperature inside rises sufficiently to liquefy the charge. The porcelain ball having a lower specific gravity than the fluid mass of glaze, floats and allows the fused glaze to flow through the hole in the bottom, into a vessel of water underneath, where it is quenched.

An arrangement has been adopted of combining four or six of these furnaces in one, so that considerable quantities of glaze can be prepared at a time; but this method is attended with the drawback of consuming a good deal of fuel. This in-

convenience has been removed by the arrangement shown in Figs. 10 and 11, in which 9-12 crucibles are mounted in three rows in one furnace. The flames from the two grates, F, F, take the direction indicated by the arrows, before reaching the chimney; and being still very hot, are utilised for warming up the next charge, heating the calciner, etc. The crucible chamber

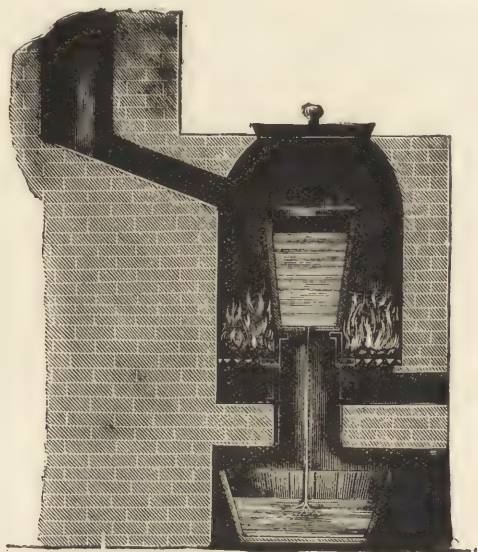


FIG. 9.

is closed at the top by a thick plate of fireclay, with holes through which the upper rims of the crucibles project. As soon as the charge in the crucibles has melted, the porcelain ball at the bottom of each floats and allows the molten mass to run out into the water tub below. The crucible lid is then taken off and a fresh charge introduced, the materials being already at a low red heat in order to prevent injury to the crucible.

The operation is carried on in this way continuously until

the cracking or other failure of the crucible necessitates an interruption of the process.

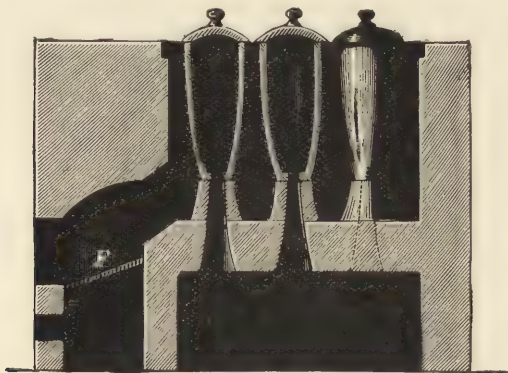


FIG. 10.

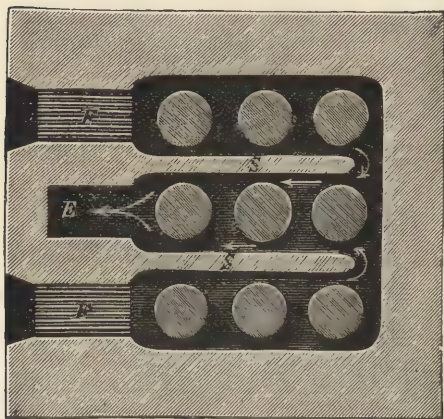


FIG. 11.

Occasionally the ball refuses to rise, although the charge has melted, so that a waste of time and fuel is incurred. This

defect, however, can be remedied by arranging the crucibles as shown in Fig. 12. Here the bottom of the crucible is provided with a conical opening, closed by a tight-fitting porcelain plug attached to an iron rod coated with an enamel of such refractory character that it will not melt at the temperature attained by the charge of glaze material. This rod is bent and passed through a hole in the crucible lid, the upper extremity being

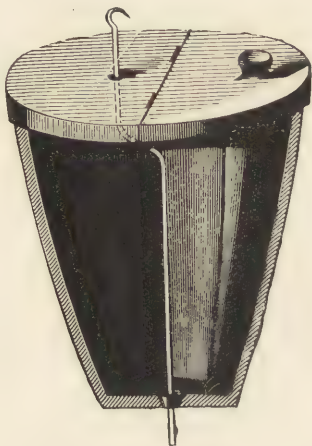


FIG. 12.

shaped like a hook to facilitate lifting. The lid is divided so that one portion can be easily removed.

As soon as the contents are believed to have melted, a rod coated with refractory enamel is dipped into the mass, and if it can be moved to and fro without difficulty, will indicate that fusion has already taken place, whereupon the valve is opened and the charge allowed to run out, the crucible being recharged at once.

Hessian crucibles, made of perfectly fireproof material, are generally used for fusing glaze masses. To prevent contamina-

tion of the glaze with iron, from the highly ferruginous material of which the crucible is composed, the latter must be lined with an extremely refractory enamel or glaze, prepared by mixing pure porcelain earth with just enough pure silica to form a mass that does not fuse below the highest white heat.

This mass is made into a thin paste with water, and applied evenly over the inner surface of the crucible, which is then slowly, but progressively, heated in the hottest part of the porcelain kiln, to melt the glaze. This method covers the inside of the crucible with a layer of smooth, hard, and lustrous glaze, which is corroded very gradually, and will not lose its gloss and become rough until the crucible has been used a great number of times for melting glaze masses.

The cracking of the crucible is generally caused by repeated rapid coolings, due, for instance, to filling it with imperfectly heated charges. In order to prolong the life of the crucibles as much as possible, care must be taken to protect them from cooling whilst in a red-hot state, and to always heat up the new charge to a very high temperature before insertion. By proceeding on these lines the durability of the crucibles can be considerably increased.

The various stages in the preparation of colourless glazes have now been described, and all that remains to be done with the fused and quenched (granulated) mass is to grind it ready for use.

The property of colourless glazes, to reveal the colour of the underlying ware on which they are fused, is not important in the case of utensils made of pure white clay. One of the chief tasks of the ceramist, however, is to impart a handsome appearance to vessels made of more or less ugly coloured material; and this can only be accomplished in one way, namely, by coating them with an opaque glaze that does not allow the colour of the ware to show through.

These opaque glazes may be coloured as desired, and in this way vessels of inferior clay can be made to look very beautiful; in fact, ordinary earthenware will assume the appearance of fine porcelain, decorated with the most beautiful colours.

Given the possession of a number of proved recipes for making glaze of any special colour, there is no difficulty in producing these glazes in any quantity, always true to shade; but, as a rule, a very large number of experiments have to be performed before this happy result is achieved in practice. These trials must of course be carried out on a small scale, with the aid of the experimental melting furnace.

THE EXPERIMENTAL MELTING FURNACE.

The disposition of this furnace must be of such a character that it will enable small quantities—usually a few ounces—of glaze masses to be fused in a short time, so that a large number of experiments can be performed in one day.

A furnace of this kind, which is found to answer admirably in practice, is illustrated in Fig. 13. It consists of an iron cylinder C, lined with fireclay, and resting on a fireclay plate. This cylinder encloses a large Hessian crucible, perforated with a number of holes a short distance above the bottom. A wrought-iron stand in this crucible serves to support a porcelain melting crucible S, which is half-filled with magnesia, and in which the porcelain, or preferably platinum, crucible containing the trial charge is embedded. By means of a handle H, of stout platinum wire, the crucible S can be lifted out of the furnace as soon as the charge is melted. The fireclay cover A is topped with an iron flue, in order to set up a strong draught in the apparatus.

The small crucible having received the trial charge and been covered with a lid, is placed in the large crucible, which is then filled with glowing charcoal or small coke through the opening B; and the cover of B being placed in position, a strong

draught is forced through the apparatus from the pipe R. This draught finds its way through the holes O, into the crucible T, and causes the fuel therein to burn vigorously. The temperature in the small crucible S soon rises to such a height as to rapidly melt the most refractory glaze. As soon

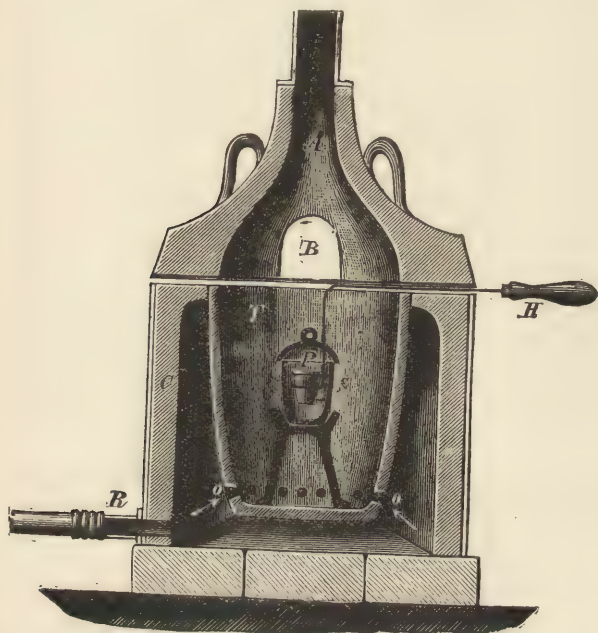


FIG. 13.

as this stage is reached, the cover A is removed, and the crucible P is taken out and thrown into water. If P is made of platinum, the molten mass falls out of itself, whilst in the case of a porcelain crucible, which cracks in the cold water, the fragments are readily detachable from the mass of glaze. A fresh crucible is placed in the furnace, filled with a new charge,

and as the furnace is now in a hot state, this second charge will usually be melted in a shorter time than the first.

Where coal-gas is available, a small gas furnace, of the type shown in Fig. 14, is preferably used for these experiments. In this case the crucible T, which is relatively tall, is bored through at the bottom, the hole being closed with a porcelain

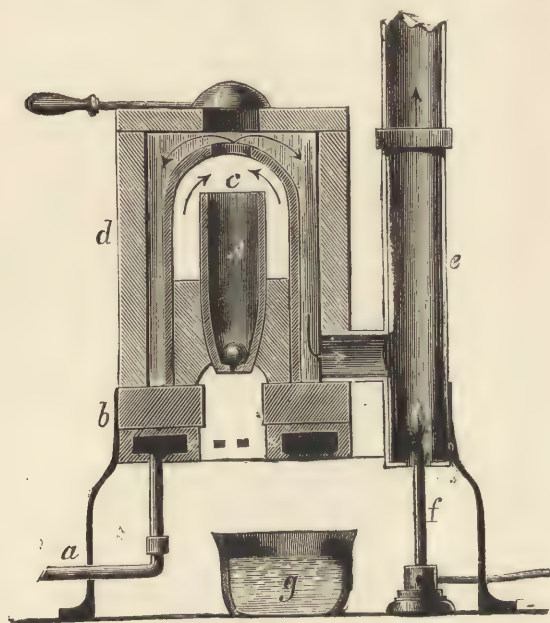


FIG. 14.

ball. The crucible is rested on a fireclay block of suitable shape, and covered with a fireclay bell *c*, surrounded in turn by a thick fireclay cylinder. The lower part of the apparatus consists of a fireclay ring, with a number of perforations on the inner side. Coal-gas is admitted through the pipe *a* into *b*, and issues therefrom in a number of thin streams through the

perforations, mixed with air, so that on ignition it burns with a very hot flame. The flames envelop the crucible on all sides, and escape through the top of the fireclay bell *c*, descending thence between the bell and the outer cylinder, in the direction shown by the arrow, and finally passing into the flue *e*. This flue is open below and is heated by a Bunsen burner, so that a powerful draught is induced in the furnace and the fusing process is complete in a very short time.

CHAPTER V.

COLOURED GLAZES.

GLAZES may be coloured in various ways. According to one method the ingredients of colourless glazes are mixed with certain pigmentary metallic compounds capable of producing definite colours. Cobalt oxide added to colourless glaze masses will furnish a blue product, which is transparent. The depth of colour depends on the amount of cobalt oxide taken, increasing with the latter; and indeed, when a large quantity of cobalt oxide is used, the coloration is so intense that the mass becomes opaque.

Analogous effects are produced by the progressive addition of ferric oxide. A yellow mass is obtained at first, changing, as the amount of oxide is increased, to red, and finally the mass is rendered opaque.

When the substance added to the colourless glaze mass is itself colourless, but, unlike cobalt oxide and ferric oxide, is not soluble in the fused mass, glazes of special character are obtained. Tin oxide is a substance which, in a finely divided state, appears white. If added in small quantities to colourless glazes, it produces a slight cloudiness, turning to milk-white when the proportion is increased, the mass at the same time becoming less and less translucent, until the stage of complete opacity is reached.

If these pure white glazes be coloured with pigmentary oxides, the resulting coloured masses differ considerably from the transparent coloured glazes. Used in this way, cobalt

oxide, for instance, will furnish a whole range of blue colours from sea blue, through forget-me-not blue to the deepest ultramarine, according to the quantity of pigment used.

The employment of pigmentary metallic compounds in conjunction with tin oxide and without this latter, enables the ceramist to produce any desired shade of colour, and all transition stages between the members of the series, and thereby turn out ware that is fully equal to hand painted, and possesses an artistic merit of its own when skilfully produced. In this connection it will be sufficient to bear in mind the beautiful majolica ware now produced in this manner at many potteries.

Owing to the ease with which the coloured glazes can be applied in various designs, by means of mechanical appliances, ware of this kind can now be made at relatively low prices, for which reason such ware has latterly been largely used for decorative purposes in building.

WHITE GLAZES.

These form the most largely used class of opaque glazes, being specially suitable for masking the ugly appearance of ware from clay of a bad colour, and making the same white. All faience ware is made from more or less coloured clay, and then coated over with a white glaze so as to produce a great resemblance to ware made from pure white clay, coated with colourless glaze.

Of late, white glazes have also been frequently used to impart a handsome appearance to ware made of very common clay. The highly artistic "porcelain" stoves now produced in many continental pottery works are made of yellow or red clay, their handsome appearance being due to the white glaze with which they are coated. The tiles used for lining hearths, fireplaces, and bathroom walls are made in a similar manner.

Another extensive application of white glaze is in the

production of opaque coloured glazes by the addition of metallic pigmentary substances; and since the shade depends on the amount of pigmentary material used, these glazes can be obtained in any desired shade. Entire pictures can be made by the aid of various coloured glazes, the appearance being equal in beauty and brightness to the best enamel paintings.

White glazes are all prepared by adding to the colourless glaze mass a corresponding amount of tin oxide, which, though a colourless substance, shares with others of the same character the property of appearing white when in a state of fine division. Hence, when a thin section of white enamel is examined under the microscope, it appears to consist of colourless particles embedded in a colourless matrix, the whiteness of the mass to the unassisted eye being due to the difference between the refractive indices of the tin oxide and other glaze constituents.

THE PREPARATION OF TIN OXIDE AND CALCINE.

The oxide may be prepared in various ways, such as oxidising pure tin with nitric acid, or by heating molten tin or a tin-lead alloy to red heat.

The first-named method is too expensive to be used for making white glazes, though it is preferable when tin oxide is to be made for use in fine enamels or ceramic experiments, since it furnishes a purer product.

The method is performed by melting tin and pouring it slowly into water, this granulation process increasing the surface of metal exposed to the action of the nitric acid, and thereby accelerating oxidation. The tin granules are placed in a large porcelain or stoneware vessel, out of doors, and suffused with concentrated nitric acid. Oxidation commences rapidly, the nitric acid being decomposed with liberation of dense brown fumes.

When the evolution of fumes has nearly ceased, the liquid is stirred with a glass rod, to detach the tin oxide from the

granules and present a clean surface of metal to the acid, more nitric acid being added, and the operation repeated until nearly all the tin is oxidised. To prevent waste of acid, it is advisable to leave a little tin in excess.

A dense white powder settles down to the bottom of the vessel, consisting of tin oxide mixed with small lumps of unaltered tin. These are separated from the oxide by levigation, and the oxide is transferred to filter paper resting on a cloth, where it is washed repeatedly with water to remove the final traces of acid. The cloth is then tied in a bundle and hung up until the oxide is quite dry and has fallen to a dense, pure white powder.

The second method of making tin oxide for glaze is based on the conversion of metallic tin into oxide by exposure to red heat in contact with air. Since the oxidation proceeds more rapidly and uniformly when pure tin is replaced by an alloy of tin and lead, such an alloy is generally used, the resulting mixture of tin oxide and lead oxide being known as "calcine." It is of course essential to know the proportions of the alloy in order to be able to make allowance for the lead oxide in calculating the addition to the glaze mass.

The absorption of oxygen during the process gives a product that is heavier than the original weight of metal taken, the proportions being as follow :—

1 part by weight of tin yields 1.27 parts of tin oxide.

1 part by weight of lead yields 1.08 parts of lead oxide.

The dissemination of particles of lead oxide in the air being inevitable in this process, the men would be exposed to the risk of lead poisoning, unless the operation be performed in an apparatus which renders the escape of lead oxide into the workroom impossible. Such an apparatus is that illustrated in Fig. 15, consisting of a shallow fireclay pan, sloping upward at one end, and resting on a strong iron plate P, heated by a fire underneath. The pan is arched over, a working aperture A

being provided in the front end, and a short flue *O* leading into the chimney *E* at the other. When the fire is burning, a strong draught is set up in the space *M* under the arch, the air being drawn from this space into the chimney, so that any dust produced in *M* is carried off, and all risk of injury to the men by poisonous dust is entirely precluded.

The operation is commenced by placing the weighed quantity

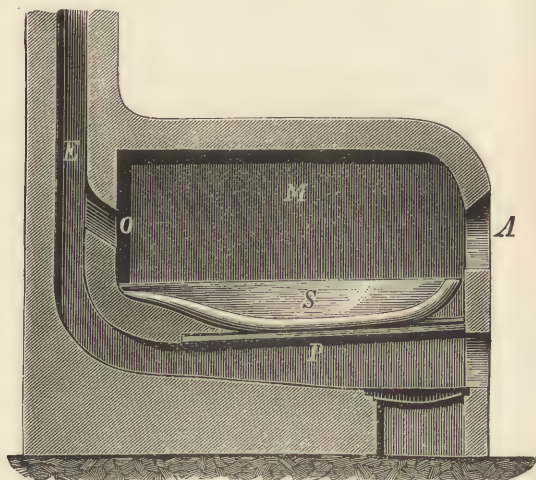


FIG. 15.

of tin in the fireclay pan, and adding the lead after the tin is melted. By building up the fire so as to produce a low red heat, the lead is quickly melted, and then mixes with the tin on being stirred with a crutch introduced through the working aperture *A*. At red heat the surface of the metal becomes coated with a layer of oxide, which is pushed by the crutch toward the rear or shallow end of the pan. This manipulation is continued until finally the whole of the metal is converted into an earthy-looking yellowish powder. After

this has been worked about with the crutch until all glimmering has disappeared, the oxide can be taken out of the pan. Since, even with the greatest care, it is impossible to prevent isolated particles of metal escaping oxidation, the crude calcine must be subjected to levigation, the recovered particles of metal being used up in the next charge.

The proportions of tin and lead taken depend on the nature of the glaze to be produced. For a glaze of high covering power the amount of tin must be increased in comparison with that used for a glaze of low covering power. In any case, however, it is advisable to prepare a glaze of the former class, since such a glaze can be applied very thinly and therefore goes further, besides showing up the contours of the glazed ware more sharply—a point of special importance when ornamented pieces are in question.

The amount of tin used with 100 parts of lead varies from 22 to 30 parts. Calcines containing the latter proportion of tin furnish a glaze of good covering power even in very thin layers.

The white produced by tin oxide in glaze is a pure, hard chalk white, which is not agreeable to the eye, except in certain circumstances. It can, however, be toned down by the use of certain adjuncts, a very small quantity of cobalt oxide, for instance, being sufficient to produce a bluish (milk) white; a very little ferric oxide will render the white creamy; chromic oxide imparts a greenish tinge, etc.

Both white and coloured opaque glazes are generally prepared as soda glazes, to secure fusibility. They cannot, however, be fused in the ordinary form of crucible with a hole in the bottom, the large content of tin oxide making the glaze viscous, so that it would run through the hole with difficulty. This defect could be overcome by using a higher temperature; but in such case the heavier tin oxide would settle down and make the lower portion of the melted charge much richer in tin oxide

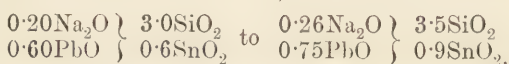
than the rest. To prevent these irregularities in the glaze, the fusing process is preferably carried on in the furnace described above.

Formerly, the glaze mass was compounded as a rule by mixing the calcine, sand and common salt together, the latter furnishing the alkali necessary to the formation of glaze. The use of common salt, however, is attended with certain evils, chief among them being the high volatility of the salt itself, a considerable amount being lost from this cause before the fusing temperature of the charge is reached. Moreover, a considerable volume of hydrochloric acid vapour is disengaged when the glaze constituents contain moisture.

The reason for the great popularity formerly enjoyed by salt in making glazes was the high price of pure soda; but now the latter can be bought very cheaply, so that salt ought to be abandoned on account of the inconvenience mentioned above.

The comminution of the fused glazes, which are drawn from the furnace as hot as possible and granulated in water is performed, in the first stage, in edge-runner mills, the product being transformed into an impalpable powder between mill-stones. This powder is stirred up to a pulp with water, and the glaze is applied to the ware by dipping or brushing on.

The composition of the white glazes usually corresponds to the limits—



The chief use of white glazes is to impart the pure white appearance of superior ware to pieces made of discoloured clay. Tiles for Swedish stoves and for use in facing walls, etc., are made of reddish or yellow clay and coated with white glaze.

NEW RECIPES FOR GLAZED-TILE GLAZES.

	1	2	3	4	5	6	7	8
Calcine	39	40	40·8	42·5*†	34	35	42·5 +	42·5†
(Tin per cent. of lead	36	36	33	50	36	38	26	20)
Quartz sand	29	26	6·4	...	28·5	32
Common salt	11·5	12·5	14·4	12	10	13	12	12·5
Norwegian felspar	9·5	...	5·6	6	8	...	6	...
Potsherds	7·5	...	2·4	5	8·5	...	5	...
Porcelain sherds	18	13
Sodium nitrate	3·5	3·5	2·8	4	3	...	4	2·5
Glaze sand (Fuersten-								
wald)	28	32·5	32·5	45
Red lead	8	7

* Banca tin.

† Half-Spanish, half-German lead.

Nos. 1, 2, 3, and 4 give pure white glazes of good covering power; 5 and 6 are not so fine; 7 gives a fine, semi-white; and 8 a pale grey.

These glazes may be coloured ivory with rutile or antimony oxide (2-5 per cent.); blue with smalt; green with chromic oxide and smalt; grey with a very little chromic oxide and manganese oxide.

GLAZES FOR WHITE TILES.

	I.	II.	III.	IV.
Calcine	100	127	23	47
Red lead	50 tin	43 tin	tin oxide	50 tin
Sand	100 lead	57 lead		50 lead
Kaolin	15	...	24	...
Porcelain sherds	100	90	36	31
Calcined soda	12	...
Common salt	10	21·5	9	11
Chalk	6	11·5
	1	...

The white glaze can be converted into a coloured one by adding suitable pigmentary metallic compounds before fusing the glaze

mass. At one time the number of colours obtainable in this way was limited, and very few of them turned out well, yellow and blue being the best. At present, however, not merely all colours, but also the most delicate modifications of tone can be produced in these glazes, and consequently this branch of ceramics has made great headway. The properly coloured ware has almost as good an appearance as porcelain, whilst being much cheaper. With regard to the decoration of white-glazed earthenware, a return has been made to earlier practice as enabling the finest colour effects to be produced.

The method adopted consists in dipping the ware in the glaze, held in a state of suspension in water, and allowing the glaze to dry in the air. The individual particles of the glaze mass adhere firmly to the ware by surface attraction, so that they cannot be removed except by scraping with a cutting instrument. Consequently, colours of suitable nature can be painted on over the glaze mass, and finally baked on to the ware at the same time as the glaze itself.

In this operation the glaze and the colour (mixed with a suitable flux) melt together, so that the contours of the design are softened by the blending of the glaze and pigment.

To secure uniformity of colour in the case of ware entirely covered with coloured glaze, it is important that the pigmentary material should be evenly distributed through the glaze mass. It is therefore preferable to add the pigmentary material, in the form of fine powder, to the other ingredients of the glaze, and to grind and melt the whole together. This method will give the desired result.

There are numerous recipes for making coloured opaque glazes, some of which are now reproduced. It may be mentioned that the shades can of course be modified at convenience, in two different ways. According to one system, the colour is deepened by increasing the amount of pigment in proportion to the other ingredients, a lighter shade being

obtained by the converse procedure. In the second system a fairly deep colour is prepared, and is then lightened by the addition of white glaze, or, in the case of colours to be applied with the brush, a certain quantity of colourless flux.

RECIPES FOR COLOURED OPAQUE GLAZES.

(*For Crockery and Tiles.*)

YELLOW GLAZES.

The handsomest pure yellow is obtained by adding antimony oxide to the other constituents of the glaze mass, the proportions being 90-95 parts of white glaze and 5-10 parts of antimony oxide.

Yellow with a reddish tinge is obtained in the same manner as pure yellow, with the difference that a certain—though in any case small—quantity of ferric oxide is used along with the antimony oxide. Very handsome intermediate shades, from pure yellow to a fairly brilliant red, can be produced by gradually increasing the proportion of ferric oxide.

Yellow green (Pistachio green) is prepared from 94-95 parts of white glaze, 2-4 parts of antimony oxide, and 2-4 parts of cupric oxide. Here, as in all cases where two pigmentary oxides are used, a great variety of shades is obtainable by modifying the relative proportions of the pigments. In the present instance shades with a yellow tinge on the one hand, and a decidedly green cast on the other, can be obtained in this way.

BLUE.

A blue shade is developed with smalt, 1-2 parts by volume of the latter being taken to 3 of white glaze.

BLUE-GREEN.

Calcine (from 1 part of tin to 5 of lead)	. 1 part by vol.
Sand	4 „

Common salt	2 parts by vol.
Cupric oxide	1 "
Smalt	0.62 "

REDDISH YELLOW.

Calcine (1 part tin, 5 lead)	1 part by vol.
Sand	2 "
Common salt	1.5 "
Ferric oxide (hammer scale)	1 "
Smalt	0.02 "

IRON GREY.

Calcine (tin 1, lead 5)	1 part by vol.
Sand	1 "
Common salt	1.5 "
Spathic ironstone (roasted)	2 "
Manganese oxide	0.1 "

PAINTING WHITE-GLAZED WARE.

As already mentioned, the best effects in painting earthenware coated with white tin glaze are obtained by dipping the ware in the glaze, allowing the latter to dry, then applying the colours (mixed with water), and finally baking the ware so that the glaze melts and the colour sinks into it to a certain depth.

Painting unbaked ware is, however, a task entailing great skill on the part of the operator, and consequently is restricted to fine ware, the general practice being to fuse the glaze on the ware first, and then paint the design, as is usual in porcelain painting, except in the case of colours fired at the highest temperatures.

To facilitate the fusing of the colours on the white glaze, they must be incorporated with a fusible glaze or flux, prepared in the following manner:—

A lead glass, with the composition PbO , SiO_2 , is made by fusing together 228 parts by weight of red lead and 60 parts

of quartz sand. The red lead, sand, and pigment must be first converted into very fine powder, then intimately mixed in suitable proportions, and melted down quickly, preferably in a crucible that has been prepared by coating the interior with a thick solution of water glass, dusting this coating over with finely ground quartz meal, and drying the whole. The crucible is next exposed to strong heat, to form a refractory glaze on the inner surface, and thus prevent any staining of the flux by pigmentary substances contained in the body of the crucible.

When the mixture of red lead, quartz sand, and pigment is fused, the mass is granulated by pouring it quickly into water, and is then ground very fine.

It is also advisable to prepare a stock of the flux without any admixture of pigment, the powdered mass being then available for lightening dark colours, its colourless nature enabling this to be done by simple mixing.

The pigments used for colour effects on white glaze are the following:—

Yellow: Potassium antimonate and ferric oxide.

Red: Red bole.

Pink to purple: Gold ruby glass.

Green: Cupric oxide or chromic oxide.

Blue: Cobalt oxide (zaffre).

Violet: Manganese oxide, manganese dioxide.

Grey: A mixture of cupric oxide, manganese oxide, ferric oxide and cobalt oxide.

Black: The same mixture as for grey, but in such larger quantity that black is obtained instead of dark grey.

Cheapness being a necessity for pigments intended for white-glazed ware, impure materials are frequently used, *e.g.* copper hammer scale in place of pure cupric oxide, and zaffre instead of cobalt oxide. But since these substances do not contain the oxides in a pure state, the colours are always less handsome and bright than when the pure materials are

employed, and the higher cost of the latter will certainly be repaid by the superior appearance of the ware.

A number of recipes for pigments to be used on white-glazed ware are to be found in various books and papers, but they are of little value to the practical man, since it is purely accidentally that they yield the desired tone. It is therefore advisable for every maker to prepare a collection of standard samples, which can be easily done by weighing out the ingredients carefully. By altering the relative proportions of the constituents, different tones of the same colour can be obtained, and it will then be easy to ascertain the exact proportions to use to obtain a given shade.

COLOURED LUSTRES.

Fine ware is occasionally decorated with lustres, which impart a handsome metallic sheen. This effect is obtained by applying to the surface of the ware a mass containing compounds of easily reducible metals, and firing the ware at low red heat in a reducing atmosphere. This causes the reduction of the metals, which then firmly adhere to the ware as a very thin film. The firing must be carried on in a muffle traversed by reducing gases.

GOLD LUSTRE.

Either of the following recipes will furnish a gold lustre :—

I.

Copper sulphide	10 parts.
Ferric sulphide	5 „
Silver sulphide	1 „
Red ochre	12 „

II.

Copper sulphide	5 parts.
Silver nitrate	2 „
Ferric oxide	1 „
Red bole	4 „

COPPER LUSTRE.

This lustre, which gives the very handsome red of polished copper, is prepared from—

I.

Copper sulphide	5 parts.
Tin oxide	2 "
Lampblack	1 "
Yellow ochre	4 "

II.

Cupric oxide	8 parts.
Ferric oxide	5 "
Colcothar	6 "
Red bole	6 "

The ingredients are mixed with vinegar and ground to a fine meal, which is mixed to workable consistency with vinegar and laid on thickly. After leaving to dry slowly, and filling up any cracks that may have formed in the mass, the ware is fired in the muffle at low red heat. The lustre mass then appears as a black, loosely adherent coating, which on removal with a brush and soft rag, leaves the handsome, metallic, golden yellow or red lustre exposed.

At present many producers of ceramic ware turn out art pottery made of comparatively inferior clay, but possessing all the appearance of good porcelain, though much lower in price. The only way in which this result can be obtained is by exercising great care in using very well-made moulds, so as to prevent the contours losing their sharpness. A second important factor consists in the employment of a perfect, white glaze of good covering power, that must be uniformly melted. Finally, care must be taken to use none but fine colours, of perfectly pure tone, for the painting. The same applies to the colours used in printing or applying transfers to the glazed ware.

GLAZES FOR FINE STONEWARE AND WEDGWOOD.

Fine stoneware belongs to the most valuable class of ceramic products, being characterised by the possession of certain properties which place it far above ordinary pottery. It is always made of fine, white-burning clay, and is so compact in structure as to be impervious to water, even in an unglazed state.

The hardness of good stoneware is so great that it will strike sparks with steel, and exhibits a fine-grained, conchoid fracture. The chief difference between this stoneware and the highest products of the ceramic art is that the former is perfectly opaque, whereas thin porcelain is translucent.

Fine stoneware is frequently glazed with earthy glazes, but more usually with transparent glazes of high lustre, especially in the case of ware intended to be coloured. In most of these glazes a portion of the silica is replaced by boric acid, and they are more lustrous, as well as more fusible and fluid when melted, than those containing only silicates. The following new recipes for these glazes are used in works making a specialty of fine stoneware *articles de luxe*. This fine ware can also be used as table ware, and should therefore never be glazed with lead glazes.

LUSTROUS GLAZES FOR FINE STONEWARE.

FRITTS.

		I.	II.
Borax	35	15
Kaolin	5	26
Chalk	12	...
Felspar	38	12
Quartz	10	30
Calc spar	8
Red lead	22

GLAZE MASSES.

	I.	II.
Fritt	20	...
Chalk	25	2
Felspar	6
Kaolin	30	2
Quartz	25	4
White lead	17

The glaze mass II. is suitable only for ware other than table ware or domestic utensils, since it is very high in lead.

CHAPTER VI.

ENGOBES AND GLAZES FOR SAME.

TO impart a different colour to ware made from clay, the colour of which is spoilt in the firing by the presence of impurities, recourse is had to an artifice known as engobage. This consists in coating the inferior ware with a mass which may be either white, or coloured in any desired way. It is not, however, feasible to employ any kind of engobe slip on any kind of ware indiscriminately, an essential condition being that both the body of the ware and the engobe should behave alike at all temperatures. Otherwise, the engobe slip after firing would exhibit the same peculiarities as are observed in the case of glazes that do not expand and contract in harmony with the ware; and, in fact, being thicker, the engobes would not only crack, but break off in lumps from the underlying ware.

In making earthenware for slip decoration, the lightest coloured clay obtainable should be used for the body, since in this case very pale engobes can be used, and ware of handsome appearance produced. In the case of lower class ware, especially cheap tiles for building purposes, there is a greater range of choice, darker coloured engobes being generally used and laid on more thickly.

The chief point in making engobe slip is to use as much as possible of the same clay as that of which the body of the ware is composed. This clay must be well levigated and then mixed with the colouring matters until the desired shade is attained.

A sample of the body is then applied to a lightly baked piece of ware and fired.

If the engobe has the proper composition it will attach itself firmly to the ware, and retain its cohesion even under the strongest fluctuations of temperature. If, however, it cracks or springs off under these conditions, it is evident that the coefficient of expansion of the engobe does not coincide with that of the body of the ware. In such event the remedy must be sought on the same lines as in the case of defective glazes, namely, by slightly increasing the proportion of refractory or fusible material, as the case may be, a few trials being sufficient to attain the desired concordance between engobe and body.

Various substances are used for colouring engobes. For making cheap white ware, especially tiles, containing no tin glaze and therefore far less expensive to produce, the engobe should be lightened in colour by additions of white clay.

If the test sample of engobe turns out too yellow in shade when baked (owing to the presence of small quantities of ferric oxide in the white clay), this can be corrected to a certain extent by adding a very small amount of smalt (the exact quantity being ascertained by experiment), which has a compensating influence on the yellow and gives the mass a fine white appearance.

For yellow, small quantities of antimony oxide are used, a very fine range of shades being obtainable by a skilful combination of antimony oxide and ferric oxide. Red bole is used for red; chrome oxide, or chrome yellow, and cupric oxide for green; smalt for blue; pure manganese dioxide for violet; a very little chromic oxide with manganese dioxide for grey; and large quantities of a mixture of manganese dioxide and ferric oxide for black. All gradations of tone can be obtained by a skilful combination of differently coloured pigments.

The engobe body is mixed with water to form a slip, and in this the ware is dipped, after having been lightly baked, since

air-dry ware lacks the necessary absorbent power. The application of engobes requires a certain amount of skill, so that all parts of the ware may be covered evenly with the engobe.

As soon as the engobe is dry, the ware may be fired, the finished pieces then having a matt surface and the same colour as the engobe. If the ware is intended to hold liquids, it must be glazed, being otherwise too porous for this purpose. Colourless glazes are always used; and those for ware or utensils destined to hold food must be free from lead compounds.

Tiles faced with white engobe must always be glazed, or they will appear dull and devoid of lustre. Very fine colour effects can be obtained with the coloured transparent glazes on white engobe tiles, especially when very richly coloured glazes are used.

POLYCHROME ENGOBES.

Since, as already mentioned, engobes can be prepared in any desired colours, they may also be employed in the manufacture of artistic ceramic products, especially mosaic pavement; and such progress has been made in this connection that mosaic patterns can now be produced in this way, surpassing the finest antique mosaics in beauty of colour and richness of design, and producing the impression of coloured carpets.

This class of decorative ware can be produced in various ways. A simple method, which gives very handsome results when carefully performed, consists in pressing the clay forming the fundamental substance of the mass, so that the design to be reproduced by means of the engobe mass is slightly impressed into the surface of the tiles.

In order to fill up the impression with different coloured engobe masses, use is made of funnels with narrow discharge apertures provided with valves for regulating the outflow of the engobe slip and stopping the same immediately when required.

Strong pressure is employed in pressing the clay tiles, and any that shrink are thrown out. To reduce the percentage of wasters, the tiles must be allowed to dry for a considerable time, and be fired at a gradually increasing temperature.

On applying the engobes, as described above, the well-baked clay tiles absorb the moisture rapidly, so that the thin slip soon thickens on coming in contact with the tiles. The quantity applied is such that the slip at first stands up in slight relief, but quickly shrinks owing to the absorption of the moisture by the tiles.

When, as is generally the case, a large number of tiles are made of the same design, each differently coloured engobe is applied by a different workman, the tiles being passed from hand to hand for this purpose. This operation having been completed, each tile is examined by another man, who repairs any defects in the engobes and makes the tiles perfect. The defects in question consist, for instance, in some part of the impressed design not having been properly filled with engobe, or the engobe having been incorrectly distributed, or again overfilled so as to project above the surface of the tile. At this stage of the process the engobes will already be fairly dry, and any surplus can be readily removed with a cutting tool, projecting parts pared down, etc.

The tiles are then ready for baking as soon as the engobes are completely dry. It is, of course, assumed that the engobes have all the same expansion and shrinkage as the tiles themselves, since otherwise they would crack, or even spring away from the substratum when fired. When the right quantities of engobe have been used, the baked tiles will be perfectly level on the surface; but if this condition is not quite realised, any slight excrescences can be removed by lightly grinding the surface.

To obtain a background of any desired colour for the design, either the tiles must be made of a suitably coloured clay body,

or, which is cheaper, of ordinary clay, that bakes red or yellow, faced with a thin layer of clay body of the desired shade. This layer may be of natural clay, if available, or else be coloured by the addition of suitable metallic oxides. The colours used for backgrounds are mostly black, grey, red, green, blue, or occasionally yellow.

Black is obtained by adding a mixture of ferric oxide and manganese oxide, the brownish tinge of which can be changed into deep black by means of a small quantity of cobaltic oxide. Grey is obtained by using a smaller quantity of the same oxides in conjunction with a white burning clay; or powdered basalt or chrome ironstone can be used when available.

Blue can be prepared in a variety of tones by the aid of cobaltic oxide, alone or incorporated with zinc oxide and alum by roasting.

Pure green is obtained by using chromic oxide, and may be shaded with cobalt oxide or yellow-burning clay. This latter is generally used for producing a dull yellow ground colour which is well adapted for showing up bright designs.

Red is obtained by means of clays that turn very dark red when baked, or else adding ferric oxide to clays that burn light red.

White-burning clays are used for white, an addition of tin oxide being occasionally given in the case of better quality ware.

Brown is obtained from red-burning clay with an addition of manganese oxide.

Care must be taken in moulding the tiles, that the clay is only just moist enough to mould, under heavy pressure, into a plate with the necessary cohesion, and one that will take a very sharp impression of the pattern die. This precaution affords the best means of avoiding distortion of the tiles in drying and baking, and presents the advantage that the dried tiles will readily absorb the moisture in the engobe slip, so

that when the latter has been applied, any excess of same can be easily removed, and the tiles will be dry in a very short time.

Recently, also, the tiles have been made by dry pressing, a method entailing the use of exceedingly strong presses, nearly always operated by hydraulic power.

In such case the method of producing coloured patterns is as follows:—The coloured clay bodies forming the pattern are applied to a base-plate by the aid of sheet metal stencils, and when this has been done, an iron frame is placed in position and filled to a given height with the finely powdered clay forming the body of the tile. An iron cover plate, fitting into the frame, is then laid on the clay, and pressure is applied. At first the pressure does not exceed 30 atmospheres, in order to allow the air to escape from between the particles of clay; but afterward the pressure is raised to at least 200 atmospheres. The tiles made in this way are distinguished by extreme hardness and cohesive power.

GLAZES PROOF AGAINST THE INFLUENCE OF CHEMICALS.

Large quantities of stoneware, in the form of retorts, boiling pans, etc., are used in chemical industries, and must, as a fundamental condition, be able to withstand the influence of chemicals such as acids and alkalis. The cost of porcelain glazes being prohibitory for such ware, the only way to secure the desired resistance is to employ a glaze consisting of a highly refractory glass, exceedingly rich in silica, glass of this type being best able to resist the action of strongly alkaline liquids.

These glazes may be applied in the usual way by firing a glaze of suitable composition on the ware; but the same object may be more easily and cheaply attained by throwing salt into the kiln at a certain stage of the baking process, the finished ware then acquiring a very thin but highly resistant film of glaze.

The reaction producing the formation of salt glaze is as follows:—

The body of the ware consists of clay that is very rich in silica. When the vapour of common salt (sodium chloride), accompanied by steam, comes in contact with the mass of glowing clay, the salt is decomposed into sodium oxide and gaseous hydrochloric acid, the former entering into immediate combination with the silica and the basic compounds (alumina) in the clay, to form an alumina-soda glass very rich in silica.

The steam, which evidently plays an important part in this reaction, is present as a constituent of the fire gases surrounding the ware in the kiln, and is always in sufficient quantity for the purpose. The salt must not be thrown into the kiln until the ware has already reached such a high temperature as to make it very close in texture, since otherwise the acid vapours would penetrate into the substance of the ware and destroy its cohesion.

When the kiln is very hot, the fire is stoked so as to burn fiercely, and a portion of the salt is thrown into the furnace. Dense vapours of salt are quickly formed, and these pass along with the fire gases into the kiln and act on the clay in the manner described. To prevent the salt vapour escaping too quickly, the damper leading from the kiln to the flue is nearly closed during the vaporisation of the salt.

The quantity of salt used depends on the size of the kiln. It is preferably added in three or four equal portions, with intervals of about half an hour between. When the last portion has been added, the kiln is closed entirely, and the glazed ware allowed to cool down.

CHAPTER VII.

PORCELAIN GLAZES.

PORCELAIN is the highest of all ceramic products, and differs mainly from all the others in being translucent when thin, without, however, being transparent in the true sense of the word. This peculiarity is due to the fact that porcelain chiefly consists of a fused, or at least highly sintered, fundamental mass in which extremely fine granules of an opaque substance are embedded. The matrix would be perfectly transparent, like glass, were it not reduced to a translucent state by the minute particles of the white substance in question, namely, kaolin. Another quality shared by all kinds of porcelain is the pure white colour of the ware, owing to the exclusive use of pure white kaolin in its production.

The innumerable experiments carried out in connection with the preparation of porcelain body, to equal that of Chinese porcelain, led to the preparation of various types of body, all entitled to be considered as porcelain, and far superior, in their characteristics, to the best Chinese ware. A distinction is drawn between two main types, namely, hard porcelain and soft porcelain.

Hard porcelain is characterised by containing a large proportion of kaolin and only very little fusible matter, generally nothing but felspar. Owing to this composition, hard porcelain possesses great heat-resisting properties, and is able to stand the highest temperatures obtainable in the kiln without melting or even sintering. It forms, when fired, an extremely hard mass, which will strike sparks with steel, and plainly reveals, under

the microscope, the presence of white opaque particles embedded in a fused glassy mass.

The better kinds of soft porcelain contain the same constituents as hard porcelain, but not in the same proportion, the fusible ingredients being present in larger amount. Consequently, this class of porcelain will not stand the same high temperatures as hard porcelain, the ware, not exactly melting, but sintering and collapsing, when exposed to the highest temperatures of the porcelain kiln. The hardness of soft porcelain is also very considerable, and its name refers not to its actual degree of hardness, but to the relative fusibility in comparison with hard porcelain. It should also be mentioned that makers of soft porcelain are now more and more frequently employing substances that do not enter into the composition of hard porcelain, the object being to reduce the cost. In consequence of these additions the product often resembles matt glass rather than true porcelain.

So far as the glazes used on porcelain are concerned, it will be evident that those for hard porcelain must be different from those for the soft variety. Great hardness and absolute resistance to high temperatures and all chemical influences being among the most valuable properties of good porcelain, it is self-evident that the glazes used for same must be of a composition giving the same properties, in point of resisting power, as the body of the ware.

Furthermore, since fine porcelain ware is nearly always decorated with colours, it becomes essential that good glaze for hard porcelain must be highly lustrous and of such a character that it can be painted on with colours.

Glazes for soft porcelain require to be fusible at comparatively low temperatures, and therefore approximate more to the stone-ware glazes, felspar glazes being unsuitable. In fact, some makers content themselves with lead glaze that melts at a very moderate heat.

GLAZES FOR HARD PORCELAIN.

In chemical composition, the glazes for hard porcelain consist of a very refractory glass, composed of silicates of alumina and lime. In certain cases an addition of alkalis or magnesia is also given.

One of the chief tasks of porcelain glaze being to preserve the pure white colour of the ware, the ingredients of the glaze must be selected with extreme care, and the raw materials be tested for the presence of iron compounds, since very minute traces of these latter will suffice to give the glaze a yellow tinge instead of remaining colourless.

The glaze may be either compounded direct from iron-free quartz sand and kaolin, plus felspar and white marble, or the mass is treated with a certain percentage of finely ground, unglazed porcelain, prepared by grinding and levigating the wasters from the porcelain kiln. Some makers also include gypsum or magnesia in the composition of their glazes.

The appearance of these glazes differs according to their chemical composition. Those rich in lime form a perfectly colourless glaze when fused, whereas those containing felspar are always more or less milky in appearance and never perfectly transparent. For certain purposes, and especially when the ware is to be decorated in colours, these cloudy felspar glazes are preferred as tending to soften the outlines of the decoration, whilst the ware coated with lime glazes has a harder look.

For these reasons, lime glazes are generally used only for ordinary tableware, which is either left quite plain or only slightly decorated with colours. The felspar glazes are almost exclusively used for fine table ware to be lavishly decorated in colour and gilding, as well as for painted art pottery.

The addition of a certain relatively small quantity of calcium carbonate or gypsum to pure felspar glaze causes the milky appearance to disappear entirely, a perfectly transparent

glass being obtained. These products are known as "mixed glazes," and are advantageously used in many works. However, since it is not easy to ascertain precisely the amount of lime necessary for producing transparency, these mixed glazes have been abandoned in many cases, and replaced by pure lime glazes, or such as contain a small quantity of alkalis as well.

COMPOSITION OF MIXED GLAZES FROM BOHEMIAN POTTERIES.

	I.	II.	III.
Kaolin	9.5	7.0	8.0
Quartz (calcined) . .	34.5	32.0	27.0
Half-baked sherds	5.0	16.5
Sherds	11.5	8.0	...
Limestone	12.0	11.0	16.5
Felspar	32.5	37.0	32.0

N.B. Half-baked sherds are those from imperfectly fired ware, the other sherds being from ware that has been exposed to the full heat of the kiln. Both are ground fine before use.

COMPOSITION OF LIME GLAZES ON ORIENTAL PORCELAIN.

Origin.	RO : R ₂ O ₃ : SiO ₂	R ₂ O : SiO ₂
Japan	1 : 1.00 : 8.91	1 : 8.04
Japan	1 : 1.00 : 10.00	1 : 8.54
Japan (Kioto) . .	1 : 1.24 : 10.34	1 : 9.00
China (Celadon) . .	1 : 0.52 : 3.82	1 : 7.35
China (white) . .	1 : 0.58 : 4.57	1 : 6.67

COMPOSITION OF FELSPAR GLAZES ON FRENCH AND GERMAN PORCELAIN.

Origin.	RO : R ₂ O ₃ : SiO ₂	R ₂ O ₃ : SiO ₂
Berlin (Old) . .	1 : 1.00 : 8.91	1 : 8.91
Berlin (New) . .	1 : 1.00 : 10.00	1 : 10.00
Sèvres	1 : 1.07 : 7.45	1 : 7.00
Limoges	1 : 1.24 : 10.84	1 : 8.74
Limoges	1 : 1.12 : 9.58	1 : 8.55

N.B.—RO = potash, soda, lime, magnesia (as fluxing medium),
R₂O₃ = alumina or ferric oxide.

COMPOSITION OF GLAZES USED IN THE ROYAL PORCELAIN WORKS,
BERLIN, FOR THE FOLLOWING PORCELAIN BODIES.

	Pure Body.	Bowl Bodies.		Insulator Body.	Service Bodies.		
		I.	II.		I.	II.	III.
Halle kaolin .	77.0	62.3	55.0	50.4	60.0	42.0	22.4
Halle clay	15.6	27.5	31.5	...	21.5	44.8
Zettlitz kaolin	18.0	17.2	16.2
Felspar .	23.0	22.1	17.5	18.1	22.0	19.3	16.6

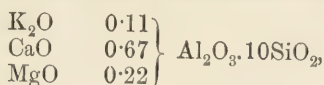
The mineral composition of the bodies is as follows:—

Clay . .	49.0	50.0	54.0	53.0	55.0	57.5	60.5
Quartz . .	28.0	28.0	28.0	29.0	22.5	22.5	22.5
Felspar . .	23.0	22.0	18.0	18.0	22.5	20.0	17.5

With regard to the application of these porcelain bodies, the so-called "pure body" is the oldest formula used in the Berlin works; "bowl body" is used specially for art products such as figures and ornaments; "bowl body II." serves for large pieces in tableware and chemical utensils (crucibles, dishes, etc.); "insular body" is for insulators; and the "service bodies I., II., and III." are employed chiefly for small pieces of tableware: plates, cups, and saucers.

The body used for large art products, such as vases, statues, and so forth, is known as "sherd body," and is made by mixing 50 parts of Halle clay, 10 parts of felspar, and 40 parts of sherds from baked porcelain.

The glaze used on all these bodies has the composition—



and is prepared from—

Hohenboka sand	165.6
Kaschka pottery earth	36.0
" " (baked)	14.0

Porcelain sherds from baked "pure body"	.	20.4
" " half-baked "	.	20.4
Marble	.	18.0
Magnesite	.	5.0

The figures given in the foregoing will enable the composition of different glazes to be ascertained when the exact composition of the available raw materials (felspar, kaolin, etc.) has been determined by quantitative chemical analysis. Once the mixture for a certain glaze is known, it can easily be made more or less fusible, in the manner already described.

The preparation of glazes for porcelain entails considerable care, since otherwise a perfect biscuit ware may be easily transformed into wasters in the glaze kiln. The first essential to be observed is that all the ingredients of the glaze must be very finely ground, a powder that will not pass through a sieve containing 10,400 meshes to the square inch, being too coarse. With the perfect appliances for crushing and grinding now at disposal, there is no difficulty in reducing the glaze ingredients to the necessary finely divided state.

In making a new glaze, it is always advisable to prepare a sample on a small scale, so as to ascertain whether it possesses the requisite properties. Should such a glaze contain over 15 per cent. of kaolin, it is liable to shrink so much in drying as to craze when fired. For this reason it is a general practice, in making glazes containing more than the above quantity of kaolin, to add the surplus in the form of strongly calcined kaolin.

Porcelain glazes are used in a state of suspension in water, and before each time of use must be stirred up with a paddle until the liquid has a milky appearance. When the glaze is left unused for some time, it sinks to the bottom of the pot, leaving the supernatant liquid perfectly clear; and when this happens, it is a matter of some difficulty to disseminate the sticky sediment in the water again, very prolonged stirring being required to effect this result.

To retard this tendency to settle down, it is advisable to add to the liquid some substance that will increase its sp. gr. and enable it to retain the fine, solid particles longer in suspension. Ammonia salts can be specially recommended for this purpose, because they are volatilised at a low temperature in the glaze kiln. Ammonium nitrate and carbonate have been tried, but the former is too dear, and is also very hygroscopic, thus greatly retarding the drying of the glaze. The carbonate is far preferable, because the greater part volatilises while the glaze is drying.

Common salt is used in many works for this purpose, and crude bay salt is said to be largely used by French potters. Salt, however, cannot be particularly recommended, since it requires a fairly high temperature to ensure volatilisation, and until that is reached is capable of exerting a detrimental effect on the chemical character of the glaze. Consequently, ammonium carbonate remains the best means for increasing the density of the glaze liquid.

The larger the proportion of water used with the glaze, the thinner will be the coating produced in dipping the biscuit ware. A difference will be observed between strongly and lightly fired biscuit, the former being less porous and therefore absorbing the glaze less rapidly, for which reason it requires to be dipped in a thicker glaze (containing less water) than that used for the more porous, lightly baked biscuit.

The thickness of the glazing liquor also depends on the chemical character of the glaze, those of the pure felspar class needing to be applied more thickly than when the mixture contains lime. The reason for this is that the felspathic glazes, when melted, attach themselves firmly to the porous ware and adhere inseparably thereto. The examination under the microscope of a section of ware with felspar glaze, clearly reveals the line of demarcation between the colourless glaze and the pure white mass of the ware itself.

With lime glazes, however, the alkaline character of the glaze sets up a chemical reaction, with the body of the ware, during the firing process, a portion of the glaze combining with the material of the ware. The resulting compound is completely fused only in the outer layers, adjoining the pure glaze, and is merely sintered in the under layers, the heat there having been insufficient to properly melt the silicates rich in alumina and silica. Hence, when lime glazes are used, the stratum of glaze actually passes into the body of the ware, and therefore a thinner layer can be applied than is the case with felspar glaze.

The pieces taken out of the dipping liquor very soon lose their gloss and resume the matt appearance of unglazed ware, the water being quickly absorbed and leaving the surface coated with the glaze powder. This, however, sticks so firmly that it can only be removed with a cutting tool. The pieces, especially those of large size, are now examined with care, any surplus glaze being scraped off, whilst any bare patches are carefully coated with glaze by means of a fine brush. Finally, the glaze is wiped off all parts on which the ware rests, such as the edges of plates and the bases of vases, to prevent the pieces sticking to the support in the kiln.

The temperature of the glaze kiln should be just sufficient to bring the glaze into a state of perfect fusion. The point at which this fusion occurs can be recognised by the previously matt ware suddenly acquiring a gloss, owing to the melting and spreading of the glaze all over the ware.

SPECIAL GLAZES FOR PORCELAIN.

In addition to the ordinary glazes for providing the matt—rough biscuit ware with a lustrous, vitreous coating—a number of special glazes are employed for the purpose of imparting peculiar features to the ware, generally in the case of *articles de luxe*.

Such special glazes may be divided into two classes: (1) coloured glazes; (2) glazes producing the appearance of crazing or cracked glaze, sometimes known as "*vieux craquelé*," a special variety being formed by "crystallised" or "crystal" glaze.

COLOURED GLAZES.

Coloured porcelain glazes can be prepared in two different ways. In the one method, ordinary colourless glaze is coloured by an addition of pigmentary metallic oxides or metallic compounds which do not undergo alteration at the glazing temperature. Since the metallic oxides used for this purpose dissolve in the glaze, they necessarily alter its chemical composition; and therefore when large quantities of these adjuncts are used, this factor must be borne in mind in calculating the composition of the glaze mass.

This can be omitted when the amount of pigmentary substance is very small in relation to the total, so that no appreciable modification of the composition occurs. Exceptions of this kind are afforded by the oxides of very strong pigmentary power, such as cobalt oxide, chromium oxide, etc., in which cases a mere fraction of 1 per cent. is sufficient to produce very bright coloration.

In firing these coloured glazes, care must be taken to prevent the fire gases coming into contact with the glaze, since the reducing action of the gases would give the finished ware quite a different colour to that it was intended to have. It is chiefly owing to the difficulties arising from this cause that preference is given in many cases to producing the colour effect by the aid of underglaze colours, instead of colouring the glaze direct.

These underglaze colours are protected from the action of the fire gases by a colourless glaze, and therefore remain unchanged in colour even when the firing is performed in a reducing atmosphere.

UNDERGLAZE COLOURS.

As the name implies, these colours are applied to the ware and fused on underneath the glaze. This method of producing colour effects, whilst applicable to porcelain, is more frequently employed in the case of faience ware. The method of preparation being generally similar to that of ceramic colours, will be dealt with at the same time as these latter, in order to avoid repetition.

CRACKED GLAZES OR "VIEUX CRAQUELÉ."

The peculiar feature of these glazes is that they are traversed by cracks in all directions, the ware having the appearance of being covered with an irregular network of fine threads. Glazes of this kind were first observed on old Chinese porcelain ware, which enjoyed a considerable popularity for a time, very high prices being paid for good specimens of "vieux craquelé" of Chinese origin.

It appears certain that the production of this effect was not intended by the makers of this old ware, but was rather the result of employing glaze of unsuitable composition. The cause of crazing has already been discussed, and the means for its prevention given. The makers of Chinese porcelain also found out how to prevent crazing; but for certain purposes they retained the use of cracked glaze, and also succeeded in imparting certain definite colours to the cracks—a point to which reference will be made later.

The attempts made by European porcelain manufacturers to imitate cracked glaze were crowned with success. All that is necessary is to modify the composition of ordinary glaze by slightly increasing the proportion of silica and decreasing the amount of alumina to a corresponding extent. At the same time the amount of lime is reduced and that of the alkalis increased accordingly. According to the researches of Lauth

and Dutailly, handsome cracked glazes can be obtained on soft porcelain.

	Ordinary Glaze.	Cracked Glazes.	
Silica . . .	66·18	79·42	69·92
Alumina . . .	14·55	11·89	18·13
Lime . . .	15·90	2·88	
Alkalis . . .	3·55	5·81	11·90

Diminishing the amount of lime in the cracked glaze has the effect of widening the mesh of the network of cracks ; but in proportion as the lime is replaced by alkalis, so the mesh becomes smaller. The fusing-point of the cracked glazes is always higher than that of ordinary glazes, and therefore they must be fired at a higher temperature than usual.

The cracks in Chinese craquelé ware occasionally exhibit differences in colour. Usually they are red, blue, or black, but sometimes the several colours are found in different parts of the same piece of ware, or running one into the other.

This variegated coloration is produced by rubbing finely levigated vermilion, cobalt blue, or Indian ink carefully into the parts to be coloured. The extremely fine particles of the pigmentary substance lodge in the cracks and colour them accordingly. The colours can be modified at convenience by rubbing-in finely levigated pigments or powdered metals. Another method, employing pigments that are unaffected by heat, consists in rubbing, say, a blue fusible colour into the cracks and then firing the ware, so as to melt the fusible colour and fix it in position in the cracks. At the same time other cracks are formed, and these can be treated in a similar manner with, say, a red fusible colour, so that the ware seems to be covered with a network of interwoven blue and red threads.

Very handsome effects can also be obtained with finely divided metal powder, *e.g.* aluminium ; a piece coated with

cracked glaze into which aluminium powder has been rubbed, exhibiting cracks with a silvery lustre.

The behaviour of sugar towards sulphuric acid in the warm can be utilised to impart a deep black colour to the cracks. With this object a fairly concentrated solution of sugar is treated with sulphuric acid in the cold, and rubbed into the cracks of the glaze. On then subjecting the ware to gentle heat in a muffle, the sugar is carbonised by the acid, and the cracks then show up as deep black lines.

CRAQUELÉ GLAZES CONSISTING OF TWO LAYERS
(IMITATION CRAQUELÉ).

This type of glazing is produced by coating the ware with a coloured glaze fired in the biscuit kiln, and then coated with a second glaze, of different colour, fired in the same kiln. The upper glaze crazes and reveals the different colour of the under layer through the cracks.

The crazing of the upper glaze can be brought about by giving it the composition that experience shows is calculated to result in crazing. For instance, a proportion of the kaolin in the glaze mass may be replaced by an equivalent mixture of aluminium hydroxide and silica, leaving the composition unchanged in other respects. Since the aluminium hydroxide parts with its water of hydration at a relatively low temperature, and shrinks considerably in the process, permanent cracks are formed, and remain after the second glaze is fired, so that the colour of the under glaze shows through.

CRYSTAL GLAZES.

Certain antique specimens of Japanese porcelain exhibit the appearance of being coated with colourless glaze with embedded crystals. Microscopical examination shows that these glazes are not of a homogeneous character, crystals being decidedly apparent in the colourless mass; and in some modern

specimens from Japan, the crystals can be detected by the unaided eye.

There is no doubt that these very handsome glazes also, like the craquelé, owed their origin to defective composition, but were afterwards designedly prepared on account of the special appearance they impart to the ware.

The occurrence of the crystals in the glaze can be explained by the phenomenon known in the glass industry as "devitrification." All ordinary kinds of glass consist of a homogeneous non-crystalline mixture of silicates. If, however, the glass be exposed for a very long time to a temperature sufficiently high to allow the fine particles of the component substances freedom of movement, silicates of definite composition are deposited in the form of crystals. These silicates have a different refractive index from that of the glass, and consequently the glass becomes either quite opaque and white, or at least very cloudy. Exactly the same phenomenon occurs in many porcelain glazes, which are in reality nothing more or less than glasses, though of a different composition to ordinary glass.

To obtain these glazes, ordinary amorphous glaze must be treated to an addition of substances that will separate out as crystals when the glaze cools. In order to enable this to be done, however, it is necessary that the glaze, fused in the ordinary way, should be allowed to cool down very slowly, so as to give the substances in question sufficient time to separate in the form of somewhat larger crystals. The formation of crystals also occurs during rapid cooling, but in such event, their size is so microscopically small that the entire mass of the glaze becomes lustreless and matt.

The formation of crystals can be induced by various substances, zinc oxide and titanous acid having been found peculiarly suitable. When zinc oxide is taken up by the glaze, a zinc silicate is formed in the melted glaze and separates in the form of crystals when cooled down very slowly.

A glaze of the following composition will furnish a very fine crystal glaze if cooled down at a sufficiently slow rate :—

Silica	57.50
Alumina	11.70
Zinc oxide.	18.00
Lime	6.70
Alkalis	6.10

To ensure successful crystallisation, however, these zinciferous glazes must be fused in an oxidising atmosphere, preferably by heating the glazed ware quickly in a muffle to such a degree that the glaze becomes very fluid, and then allowing the closed muffle to cool down as gradually as possible.

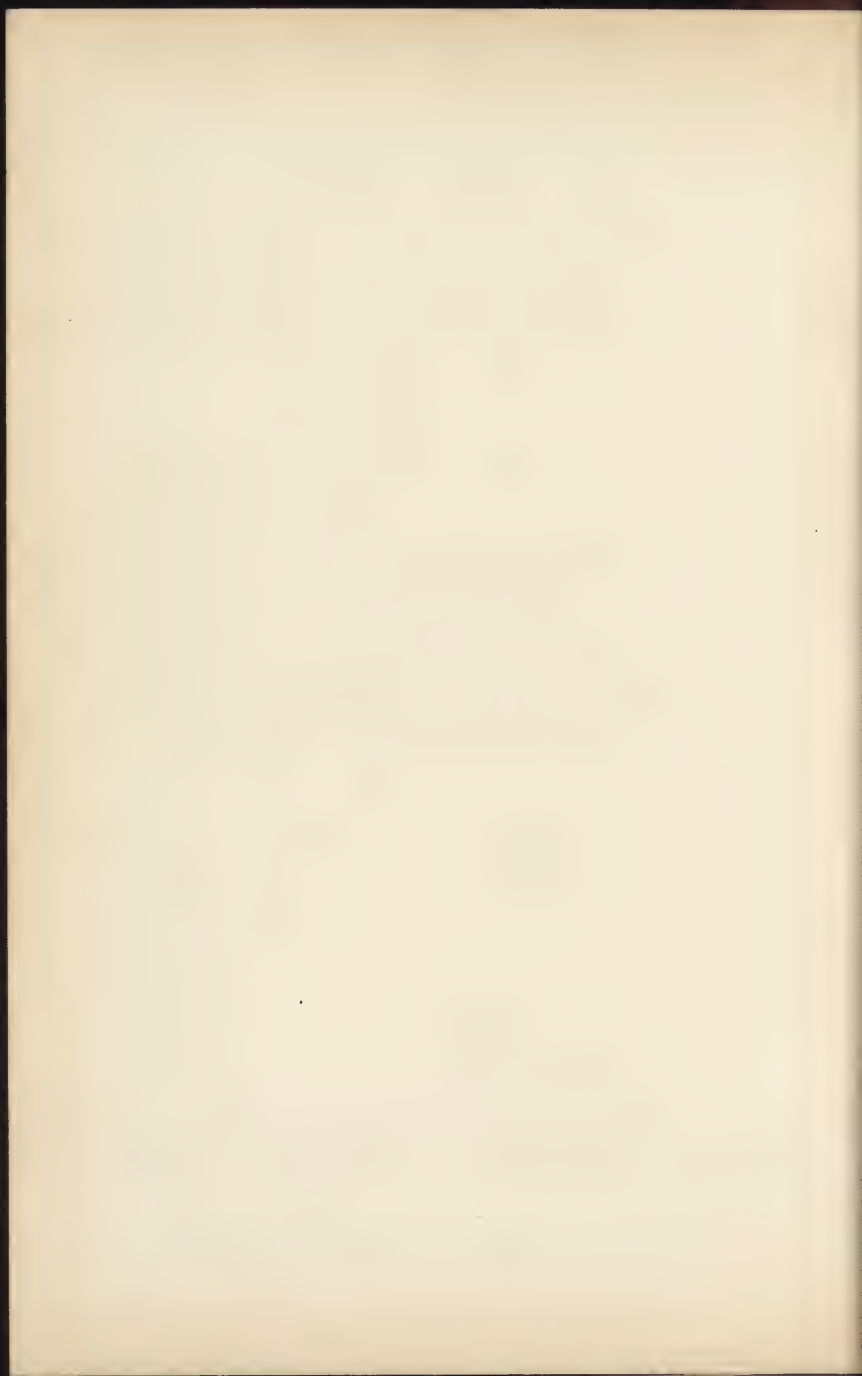
According to a method elaborated in a porcelain works at Copenhagen, crystal glaze is prepared in the following manner. The porcelain ware is first coated with a refractory glaze, which is fired in the usual manner, care being taken to apply a fairly thick coating; and on this is brushed a thick layer of a mixture of silica and zinc oxide, the latter in excess.

When this second coating is dry, the ware is again fired in a sharp fire, care being necessary to protect the ware from all contact with a reducing atmosphere. The fired glaze will be found to be interspersed with crystals of zinc silicates. It is probable that a reaction occurs, in the sharp fire, between the original glaze and the second coating, a basic zinc silicate being then deposited from the homogeneous glaze. These glazes may also be coloured by adding small quantities of pigmentary metallic oxides, such as cobalt for blue, cupric oxide for greenish shades, chromic oxide for green, etc. In such case, the crystals, which are usually darker in colour than the rest, will show up still more handsome and clearer than in uncoloured glazes.

The finest crystalline glazes, however, are obtained by using titanitic acid. The usual plan is to employ a zinciferous glaze, which, however, requires firing in an oxidising fire. When it

is necessary to work with a reducing fire, the zinc oxide is replaced by a corresponding quantity of magnesia.

Crystal glazes can be made that do not need such high firing temperatures as the foregoing. For this purpose a fusible lead glaze—specially recommended for soft porcelain—is employed, with an addition of titanitic acid. These glazes may also be coloured, and are easily fired on the ware, forming a very handsome glaze interspersed with crystals.



PART II.

CERAMIC COLOURS.

CHAPTER I.

GENERAL REMARKS ON CERAMIC COLOURS.

THE pigments used in the ceramic industry, in the widest sense of the term, must evidently consist of bodies that will stand the high temperatures used for firing the coloured glazes, without undergoing alteration. It follows naturally that all organic colouring matters are out of the question, these being destroyed at relatively low temperatures. It is true that organic pigments are used for one class of ware—"siderolith" ware; but in this case the colours are not exposed to heat at all, being merely stirred up with lacquer varnish and applied to the surface of the finished ware, from which they can be scraped off again with a sharp knife—an operation impossible with ware that has been coloured in the glaze, the colour in such case forming an integral part of the glaze itself.

The pigments generally used for ceramic purposes are either metallic oxides or compounds of such oxides with metallic acids, or else consist of noble metals—gold, platinum, or silver—attached to the glaze by suitable means.

It is a well-known fact that all clays—except the white-

burning kaolin and pipeclay—change their colour in burning. The colour of burnt clay usually ranges between pale yellow and brown, or light to dark red, owing chiefly to the presence of compounds of iron or manganese in the crude clay. Whilst the intensity of the colour depends on the amount of the iron or manganese compounds present, it is also influenced by other ingredients of the clay, such as lime and magnesia, and also by the temperature at which the clay is fired.

The great variety of this coloration can be easily seen in the case of the commonest of all ceramic products, namely, bricks. These, when made of marly clay, and especially when baked in badly built kilns, in which some of the bricks are overburned and others imperfectly baked, often exhibit a variety of colours, from pale leather brown, through all stages of brown and red, to black.

Formerly, when little was known of the substances causing the development of colour in baked clay, it was naturally assumed that every clay had its own peculiar colour, and could therefore be used only for that coloured ware. In order to obtain ceramic products of a different colour, the practice arose of covering the ware with a coating which would impart the desired shade and at the same time remove the porosity of the burned clay—in other words, the ware was coated with glaze.

It may have been the result of accident that powdered mineral pigments were first introduced into glaze masses and furnished definitely coloured glazes in the kiln, to be afterwards added for the express purpose of producing the same result, thus forming the commencement of the technology of ceramic colours.

The pigmentary principles in these minerals are seldom present in a pure state—pure red hæmatite and pure manganese dioxide being two rare exceptions—but are mostly associated with other substances influencing the colour. Thus, for

example, chrome ironstone, in addition to the pure green pigment chromic oxide, contains ferric oxide, which itself gives a brownish-red colour; cobalt ores invariably contain an admixture of nickel, which gives the blue a yellowish tinge. For this reason it is impossible to obtain perfectly pure colours by merely adding pigmentary minerals to the glaze, the beauty of the colours being always more or less a matter of chance.

The progress of chemical science first enabled the study of ceramic colours to attain the stage at which it became possible to develop perfectly pure colours in glaze, and to obtain any desired shade and mixture of colour, so that, at the present time, the fairest gradations in colour can be produced with ceramic pigments just the same as with oil and water colours.

The great advance made in this connection can be easily appreciated by a comparison between the painting on antique majolica ware and modern porcelain. In the former case translucent colours are a rarity, and the colours are seldom pure in tone.

It is true that rich colour decorations are often seen on old Chinese porcelain; but here, too, the colours are almost invariably opaque, and the palette of the Chinese artists was short of a whole series of colour shades. The same applies also to some extent to old Japanese porcelain.

In Europe, ceramic painting has been modelled on another branch of art to which it is closely related, namely, glass painting. As a matter of fact, the difference between the two is so slight that in some instances the same colours are used in both; and in principle they are alike, certain mixtures of ingredients containing pigmentary substances being fused on to the glass in one case, and on to the glaze in the other.

The rapid development of chemistry from the commencement of the nineteenth century led to great advances in the technology of colours, and enabled the pigments used in ceramic painting to be obtained in a perfectly pure state.

From these pure colours it has been found possible—as already mentioned—to prepare mixtures exhibiting all the gradations of colour that can be obtained with any painting medium. The high resisting powers of the ceramic colours and their support (*e.g.* porcelain) gives the paintings executed in this manner an almost unlimited durability, since they cannot be destroyed except by purely mechanical influences. Paintings on porcelain executed on present-day lines could probably remain buried in the earth for a thousand years without injury to their beauty of colour.

CHAPTER II.

THE CERAMIC COLOURS IN PARTICULAR.

IT has been stated earlier that certain minerals (chiefly ores) were long used to produce colour effects both in the body of the ware and in the glaze. These minerals are still employed for the same purpose, but their use is now restricted to common ware, experience having shown that of two pieces made of the same clay, the one coated with a beautifully coloured glaze will have by far the higher selling value.

Since it is now easy to procure ceramic pigments in a perfectly pure state, every potter should—for the above reason—use pure coloured glazes only, and pure pigments for painting.

The following is a list of the oxides constituting the foundation of the pigmentary principle in all coloured glazes and ceramic colours:—

Ferric oxide, for yellow, red, brown, and in some mixtures also for black.

Manganese oxide, for violet, brown, and in mixtures for black.

Cupric oxide, for green, bluish green, and certain green shades clearly distinguishable from pure green.

Cobaltic oxide for all shades of pure blue.

Chromic oxide for pure green and also for red.

Nickel oxide for brown.

Uranium oxide for yellow.

Gold (in a certain form) for red—rose red to purple.

Platinum and iridium for grey and black.

The substances are the basis of the ceramic painters' palette, and can be made, by suitable intermixing, to yield the greatest variety of tones.

Another class of substances is used in ceramic painting to develop certain shades of colour and also as fluxes; but these will be dealt with when we come to describe the preparation of the individual colours, and we will now only illustrate the action of such adjuncts by an example.

Cobaltic oxide colours glaze pure blue, from the palest water blue to the deepest ultramarine; and tin oxide, though non-pigmentary of itself, produces a fine white when mixed with glaze. By mixing the two together in various proportions we obtain blue colours having similar properties to the enamel colours; they cover well (not allowing the substratum to show through), and form a blue resembling that of the forget-me-not or turquoise.

The composition of ceramic colours is varied according to the purpose to which they are to be applied; and they are classified into groups according to the value of the ware to be decorated. For ordinary pottery, the impure pigmentary minerals are used; *e.g.* crude ferric oxide for red, manganese oxide for brown or violet, chrome ironstone for black, and so on. In the case of finer ware, *e.g.* good stoneware, purer pigments must be taken in order to produce handsome colour effects, the same pigments being also used for engobes and underglaze colours (so called because they are applied to the ware before glazing).

Naturally, only the purest colours are used for the third and most valuable class of ceramic products, namely, porcelain. These colours are divided again into: sharp-fire (*grand feu*) colours (few in number), which are applied and fired before glazing; glaze colours, in which pigments are mixed with the colourless glaze; and muffle colours, the latter re-

ceiving their name from being fired in muffle furnaces at a relatively low temperature. The muffle colours, which also comprise the noble metals—gold, platinum, and silver—and the lustre colours, are always applied and fired over the glaze. Owing to the free hand allowed in shading these colours, and the possibility of obtaining with them any desired range of tones, they lend themselves most freely to artistic application. It is unnecessary to say that the colours must be perfectly pure to be suitable for this purpose.

CHAPTER III.

PREPARATION OF THE PURE COLOURS.

IT is advisable to begin this sketch of the preparation of ceramic colours with a description of the various methods by means of which the perfectly pure pigmentary substances can be obtained. The practical potter will then be able to decide whether and for what purposes he will use these pure pigments. The substances chiefly in question are the oxides of iron, chromium, cobalt, nickel, manganese, and copper, together with chemically pure gold and gold preparations.

THE PREPARATION OF PURE FERRIC OXIDE.

Ferric oxide is frequently found in nature, and occurs almost chemically pure in some minerals, *e.g.* specular iron ore and red hematite. Consequently, a product suitable for the preparation of ceramic colours can be obtained by grinding one of these minerals to a very fine powder and levigating the latter. Owing to the great hardness of the raw material, this method is expensive, and the product is never so fine as when the ferric oxide is prepared by artificial means.

For this purpose use is generally made of the cheap commercial salt, ferrous sulphate or green vitriol, by dissolving it in water and treating the filtered solution with nitric acid in a large vat, so as to oxidise it to ferric sulphate. At the end of a few hours, ammonia is added so long as a precipitate continues to form. This very bulky precipitate, consisting of ferric oxide, has a handsome reddish-brown colour, and

settles down fairly quickly. The supernatant liquor is run off through tapholes arranged at different levels in the walls of the vat, and the sediment is repeatedly washed by stirring it up with fresh quantities of water, after which it is collected on a filter cloth and dried artificially or by prolonged exposure to the ordinary temperature. The dried precipitate, consisting of ferric hydroxide, has a reddish-brown colour, and can be transformed into pure ferric oxide by moderate calcination, a high temperature spoiling the purity of the red colour. In fact, by gradually raising the oxide to very high temperatures, its characteristic colour changes into cherry red, purple, brown, and violet, the alterations being due to modifications in the structure of the fine particles of the oxide under the influence of heat.

A very beautifully coloured ferric oxide, known as Vogel's iron red, is prepared by treating a solution of pure ferrous sulphate with one of potassium oxalate so long as a precipitate forms, and then washing and drying this latter, followed by gently heating it in a shallow porcelain dish. At a certain heat the contents of the dish begin to glow, and are gradually converted into a very finely divided ferric oxide of a beautiful red colour.

Common grades of iron red and other iron colours can be prepared from the iron hammer scale thrown off during the forging of white-hot iron. This scale consists of ferro-ferric oxide, and can be transformed by calcination and levigation into a fairly pure ferric oxide, highly suitable for making cheap glazes, whereas only the artificial oxide will do for finer purposes.

THE PREPARATION OF CHROMIC OXIDE.

Chromic oxide is one of the most important ceramic colours, being the only substance that furnishes a perfectly pure green capable of standing the sharp fire of the kiln, and therefore

suitable for underglaze colour, as well as for incorporating with the glaze and for applying to the surface of the latter as a muffle colour.

Pure chromic oxide can be prepared in several ways. A method frequently practised consists in intimately mixing equal parts of potassium bichromate and sulphur, both very finely powdered, and exposing the mixture to low red heat in a porcelain crucible. The fused mass is crushed, and washed repeatedly with water until all the soluble matter has been attracted, the dried residue then forming a dark green powder consisting of pure chromic oxide.

Another but more expensive method is by carefully heating mercuric chromate in a porcelain crucible, the salt decomposing, with liberation of volatilised mercury, and leaving a chromic oxide of very handsome colour.

To prepare chromic oxide by the wet method, potassium bichromate is dissolved in hot water, and the solution is treated with sulphuric acid, followed by alcohol added carefully in small quantities. The liquid rapidly grows hot and changes from a fine red colour to violet. On treating the cooled liquid with caustic soda, a greyish-blue precipitate of chromic hydroxide is formed; and this is thoroughly washed, dried, and calcined. The resulting chromic oxide varies in depth of colour according to the temperature of calcination, but this makes no difference so far as our purpose is concerned, the colours being always fired at a definite temperature.

THE PREPARATION OF COBALT OXIDE.

This oxide is the only substance furnishing a pure blue suitable for ceramic colours. It could be prepared from the natural ores in which it is contained, but the separation of the other metals present is such a troublesome task that it is usually left to the chemical manufacturer, and the pure commercial cobalt salts are used in preference. The chief of

these salts are the chloride and nitrate, the oxide being prepared by dissolving one of them in water, treating the solution with caustic soda so long as a precipitate continues to form, and drying the latter after repeated washings with water. The residue is then strongly calcined in a porcelain crucible, and furnishes a deep black powder consisting of pure cobalt oxide.

THE PREPARATION OF MANGANESE OXIDE.

This oxide, which is very important for brown, violet, and black colours, is also most simply prepared from a commercial salt of manganese, manganous sulphate being preferred as obtainable perfectly free from iron. The fine red crystals of this salt are dissolved in water, precipitated with caustic soda, and the precipitate of manganous hydroxide is well washed, dried, and calcined.

THE PREPARATION OF NICKELOUS OXIDE.

This oxide is prepared from nickelous sulphate, which is obtained in commerce in a perfectly pure state as green crystals, the method adopted being the same as that just described, namely, precipitating the dissolved nickelous sulphate with caustic soda, and washing, drying, and calcining the precipitate.

THE PREPARATION OF CUPRIC OXIDE.

For this purpose a copper sulphate perfectly free from iron compounds is required, on which account the finest guaranteed iron-free commercial brands must be employed. A very fine grade of this salt is obtained, for example, in mints where gold is extracted from old silver coins by dissolving them in boiling sulphuric acid. The gold settles down as a brown powder, whilst the liquid containing the dissolved silver is decanted and the silver recovered by displacement with copper. The resulting solution of copper sulphate is perfectly free from iron compounds.

The copper sulphate is dissolved in hot water and treated with caustic soda till precipitation ceases. The black precipitate of pure cupric oxide is collected on a filter, washed with hot water and dried.

THE PREPARATION OF ANTIMONY OXIDE.

Antimony oxide is largely used as an adjunct in the preparation of ceramic colours, and must be pure for the finer grades. It is obtained by finely powdering native antimony trisulphide (grey antimony ore) and boiling the same in crude hydrochloric acid until no more is dissolved. The liquid is poured on a filter placed above a vessel containing about 300 vols. of water to 1 vol. of the solution. This dilution of the solution causes the latter to deposit a brilliant white dense powder consisting of antimony oxychloride, which is transferred to a porcelain basin, suffused with an aqueous solution of sodium carbonate and heated to boiling. Carbon dioxide is liberated and sodium chloride formed, which passes into solution, leaving the powder transformed into pure antimony oxide, which is filtered, washed, and dried.

This roundabout method is not followed in the case of inferior colours, the finely pulverised grey antimony ore being merely spread out thinly on a strongly heated iron plate, and thereby reduced to a white mass of fairly pure antimony oxide, which is repeatedly levigated, in order to eliminate the undecomposed antimony ore.

The pure oxides obtained in the above manner are either used alone or mixed together to produce various shades of colour.

Use is also made of certain salts possessing characteristic colours; but owing to the high temperatures necessary in firing all ceramic colours, it follows that only such salts as are fire-proof, *i.e.* will stand high temperatures without decomposition, will be suitable. Consequently the choice is restricted almost

entirely to phosphates, the salts of chromic and stannic acids, and certain silicates.

MANGANESE PHOSPHATE.

This preparation, which is used for certain peculiar brown to violet shades, can be obtained by precipitating a solution of 42 parts of manganese sulphate with 36 parts of sodium phosphate and a solution of 5 parts of sodium carbonate, the precipitate being then washed, dried, and slowly heated to redness.

COBALT PHOSPHATE.

This compound is prepared by precipitating a solution of cobalt nitrate or chloride with sodium phosphate and sodium carbonate (as in the case of manganese phosphate), and washing, drying, and gently calcining the precipitate. In calcining these precipitated colours, care must be taken not to heat them to actual fusion, as in such case the troublesome operations of powdering and levigation would have to be gone through, and they would not furnish such a finely divided product as that obtained by precipitation—a point of considerable importance.

COPPER PHOSPHATE.

Thirty-seven parts of iron-free copper sulphate are dissolved in water, and this solution is mixed with one of 35 parts of sodium phosphate and 5 of sodium carbonate. The resulting precipitate is treated as in the two preceding cases.

COBALT CHROMATE.

This salt is obtained by dissolving 155 parts of (anhydrous) cobaltous oxide in water and treating the solution with one containing 97 parts of potassium chromate (yellow commercial chromate), the precipitate being well washed, dried, lightly calcined, and rewashed.

BARIUM CHROMATE.

A solution of 104 parts of barium chloride is treated with one of 98 parts of potassium chromate, and the precipitate washed and gently calcined. In this way a handsome yellow product is obtained; but by employing higher temperatures and longer heating, the colour gradually acquires a greenish tinge, and can finally be transformed into a decided canary green.

CHAPTER IV.

UNDERGLAZE COLOURS.

AS their name indicates, these colours are applied to the ware previous to glazing, and are subsequently covered by the glaze. Owing to the possibility of the glaze reacting chemically on the colours at the high temperatures of the kiln, the underglaze colours must always be prepared from pure oxides and salts that are capable of withstanding such action.

The pigmentary substances are not used alone as underglaze colours, but are usually mixed with 20 per cent. of their weight of stoneware glaze, or the same quantity of boric acid, and then recalcined. The mass must then be washed with water so long as any soluble materials are extracted. These materials usually consist of small quantities of sulphates, which, if allowed to remain, would cause the colours to blister in the kiln.

All the colours mentioned below are suitable for underglaze colours.

YELLOW UNDERGLAZE COLOURS.

TITANIUM YELLOW (RUTILE YELLOW).

The fundamental material of this handsome yellow colour is the mineral rutile, consisting of impure titanitic acid. To obtain the colour (which consists of zinc titanate) equal parts of rutile and zinc oxide are ground to an impalpable powder in a wet mill, the mixture being then strongly calcined after drying.

Attempts made to prepare this colour from chemically pure titanitic acid and zinc oxide are unattended with success, the

small proportion of iron present in the rutile being apparently essential to the development of the colour.

ANTIMONY YELLOW.

This pure light yellow colour is prepared from the following constituents:—

Lead nitrate	73 parts.
Antimony oxide	33 "
Alumina	12 "
Common salt	100 "

These substances are thoroughly mixed by prolonged trituration and are then fritted, the fritt being powdered and well washed. In this way a pale bright yellow is obtained, which, however, is too fluid when melted, and would therefore sink into the surface of the ware when fired. To remove this defect, the finished colour is mixed with up to about one-third of its own weight of calcium stannate, which makes it more refractory. The calcium stannate is prepared by wet grinding 75 parts of tin oxide and 30 of calcium carbonate (white marble), and then drying and strongly calcining the mass. The addition of small quantities of ferric oxide to pure antimony yellow deepens the colour and imparts an orange tinge.

ANTIMONY ORANGE.

This is prepared from—

Red lead	50 parts.
Antimony oxide	33 "
Ferric oxide	18 "
Potassium nitrate	25 "

The finely powdered mixture of the above ingredients is calcined, ground, and washed. Owing to the great fusibility of the colour, it is mixed with calcium stannate, as in the case of antimony yellow.

RED UNDERGLAZE COLOURS.

PINK COLOURS.

These colours are among the most important of all used in ceramics, inasmuch as they can be prepared in four different grades, and will furnish all imaginable intermediate gradations from pure red, through purple red, to deep violet. In chemical composition, pink red consists mainly of a combination of tin oxide and lime, but the various gradations of colour are produced by the incorporation of other compounds suitable for the purpose in view.

The higher the proportion of lime, the brighter red the colour. An addition of boric acid to the mass, or coating the colour with a borate glaze, gives the pink a bluish tinge. When lime is entirely omitted, the colour is a pure violet, so that highly divergent tones can be obtained with this very stable preparation.

PURE PINK RED.

This colour which may be regarded as the real typical pink, is prepared in the following manner.

Pure tin oxide (preferably that obtained by treating tin with nitric acid and calcining the product) is strongly calcined, and then mixed with the other ingredients, which have previously been ground very fine separately.

The following proportions are used :—

<i>finely powdered</i> <i>chalk</i>	Tin oxide (calcined)	maible	.	.	.	100 parts.	<i>6 1/4</i>
	Calcium carbonate		.	.	.	50 "	<i>3 1/2</i>
	Quartz		.	.	.	36 "	

Powdered pure white marble is used, and the quartz sand must be quite colourless, and therefore free from iron. The intimate mixture of these substances is stirred up with a hot-saturated solution of 6 parts of potassium bichromate and 8 parts of borax, and then heated to dryness in a porcelain dish,

with frequent stirring. The dried mass is ground very fine in a porcelain mortar, and very strongly heated in a crucible, care being taken that no reducing gases have access to the mass, since this would spoil the colour.

This evil may be avoided by placing the charged crucible in a larger one and packing the intermediate space with manganese dioxide. This liberates oxygen at calcination temperature, and thus precludes the admission of reducing gases to the contents of the inner crucible. It is desirable to perform the calcination in a furnace in which a strong white heat can be developed, a high temperature of this kind being essential to the production of a good coloured preparation of brilliant appearance.

The pure red colour of the above preparation can be tinged bluish red by omitting the quartz from the mixture and using only tin oxide and calcium carbonate.

PINK (BLUISH RED).

Tin oxide (strongly calcined)	.	.	70 parts.
Marble	.	.	23 „

This mixture is treated as described for pure red, followed by an addition of 3 parts of potassium bichromate and 4 of borax.

PINK (ROSE RED).

A rose-coloured pink is obtained with the following formula :—

The powdered ingredients mentioned below are ground extremely fine, and the mixture is exposed to the strongest white heat. The resulting mass is reground, and then lixiviated with boiling water until all the soluble matter has been extracted.

Tin oxide	60 parts.
Calcium carbonate (marble)	31 „
Quartz	3 „
Kaolin	3 „
Lead chromate (pure chrome yellow)	3 „

PINK (PALE ROSE RED).

This is obtained when the rose red preparation above is worked into a homogeneous mixture, by grinding, with stoneware glaze and calcium carbonate. The following proportions are generally taken :—

Rose red (as above)	44 parts.
Stoneware glaze	44 „
Powdered marble	12 „

VIOLET PINK COLOURS.

By means of the pink colours, all gradations from pure red, through purple, to deep violet can be obtained, the usual preparations employed containing cobalt oxide as pigmentary ingredient. The following colours are most in use :—

CLOVE PINK.

Fifty-five parts of tin oxide and 40 of calcium carbonate (marble) are intimately mixed by grinding, the powder being then stirred up with a solution of 5 parts of potassium chromate in water, drying the mass and exposing it to the strongest white heat. The calcined mass is finely ground, and treated with hot water until all the soluble matters are extracted.

LILAC (PALE VIOLET).

Tin oxide (strongly calcined)	50 parts.
Potassium bichromate	3 „
Borax	20 „

The bichromate is dissolved, with the borax, in a minimum of hot water, then mixed with the tin oxide and strongly calcined, this operation being followed by complete lixiviation with hot water.

PALE VIOLET (VIOLET UNIQUE).

This peculiar shade of violet is best obtained by the formula :—

Tin oxide	100 parts.
Boric acid (pure)	10 „
Cobalt oxide	1 „
Lead chromate	1½ „

The finely powdered ingredients are intimately mixed by prolonged trituration, and the mixture after strong calcination is leached with hot water. Next, 80 parts of this mass are mixed with 20 parts of fine white lead and fused, the product forming *violet unique*.

PINK PURPLE.

Cobalt oxide	60 parts,
Quartz	15 „
Stoneware glaze	25 „

are intimately mixed in the mill, strongly calcined, and reground as finely as possible. The resulting blue mass is mixed with pure pink red in the following proportions :—

Pure pink red	92 parts,
Blue mass	8 „

the mixture furnishing a very handsome purple red. To impart a more violet tinge the blue mass is slightly increased ; but great care must be exercised, on account of the strong pigmentary power of the cobalt oxide, or the colour will be turned to violet if a certain limit be exceeded.

THE RED GOLD COLOURS.

By using the compound, gold trichloride, the preparation of which will be described in dealing with that of chemically

pure gold for the purposes of ceramic painting, very handsome red colours can be obtained, which can be shaded in all gradations between dark purple red and the most delicate rose red. The pigmentary principle in these colours is gold, though the exact form in which the metal is present is not known.

GOLD PURPLE RED.

This preparation is obtained in the following manner:—

Ninety parts of finely levigated white kaolin are distributed in water, heated to boiling and well stirred, the whole being then strained through a fine hair sieve to remove any lumps of kaolin.

While the mixture is kept in constant motion, a solution of gold trichloride (containing 10 parts of chemically pure gold) is added, followed, drop by drop, by an aqueous solution of sodium carbonate, until the liquid has a decidedly alkaline reaction, *i.e.* turns red litmus paper blue. A solution of 20 parts of grape sugar in water is next added, and the whole is boiled strongly, with constant stirring, the water lost by evaporation being replaced from time to time. After boiling has continued for about half an hour, the whole mass will have acquired a deep purple red colour, whereupon it is allowed to cool.

The contents of the vessel are transferred to a cloth faced with filter paper, and suffused repeatedly with boiling water, until the latter ceases to extract any soluble matter. When thoroughly dried, the mass is calcined, rewashed, and ground.

Working in the same way, but with proportionately reduced quantities of gold, the resulting colour will be correspondingly lighter, a mass containing only 2 parts of gold to 98 of kaolin being pale rose red.

THIVIER'S RED (FLESH TINT).

This very handsome flesh tint colour consists essentially of an aluminium-iron silicate of the composition—

Silica	88 parts.
Alumina	3 „
Ferric oxide	7 „

It may be prepared by mixing a solution of aluminium sulphate with one of ferric sulphate in proportions furnishing the above ratio between the oxides, and then treating the liquid with a solution of water-glass so long as a precipitate continues to form. This is carefully washed, dried, and strongly calcined.

Increasing the amount of ferric oxide in the liquid deepens the colour of the resulting red; and conversely a lighter shade is obtained by increasing the proportion of the alumina. This red may be used as an underglaze colour, but not under a strongly acid glaze, or the compound will be attacked by the silica or boric acid present, a yellow colour being then obtained owing to the formation of ferric silicate or ferric borate.

IRON RED.

True iron red—which is different from Thivier's red—always consists of a mixture of ferric oxide and alumina. The relative proportions of the ingredients may be altered at convenience, but an increase in the content of ferric oxide will furnish a more brownish red, whilst paler reds follow any increase of alumina. It is, however, advisable to prepare a standard “iron red” according to a certain formula, namely, the following:—

Twenty-eight parts of pure ferrous sulphate are dissolved in distilled water and stirred, nitric acid being meanwhile poured in until the liquid is no longer dark brown in colour

but reddish yellow, thus indicating the complete conversion of the ferrous oxide into ferric oxide, the liquid being then mixed with a solution of 190 parts of potassium alum in water.

Caustic ammonia is next added so long as a precipitate continues to form, the latter being afterwards washed with hot water on a filter until no more soluble matters are extracted. The dried mass is gently calcined and mixed with ferruginous (yellow) glaze, in the proportion of 30 parts of the latter to 70 of the iron-alumina mass. The mixture is ground as finely as possible, and is then ready for use.

GREEN UNDERGLAZE COLOURS.

Chromic oxide is always used for pure green, and, without any admixture, except ground stoneware glaze, for the dark shades, other tones being obtained by the addition of various oxides.

DARK GREEN.

Chromic oxide	75 parts.
Nickelous oxide	150 "

This mixture furnishes a green with a certain yellowish tinge.

LIGHT GREEN, ACCORDING TO TENAX.

Potassium bichromate	36 parts.
Calcium chloride (anhydrous)	12 "
Quartz	20 "
Marble	20 "
Fluor spar	12 "

The quartz, marble, and fluor spar are ground on a wet mill, and after the water has been drained off, are stirred up with the dissolved bichromate and calcium chloride. The pap is heated, with occasional stirring, until dry, after which it is finely powdered and exposed, in a porcelain crucible, to the highest temperature obtainable in the furnace.

ZEISSIG GREEN.

Barium chromate	50 parts.
Marble	40 „
Boric acid	25 „

The ingredients are intimately mixed, and then exposed to the highest temperature attainable.

BLUE UNDERGLAZE COLOURS.

The pigmentary principle of all the blue colours used in ceramic decoration is cobalt oxide, either alone or in association with other oxides. By taking suitable proportions of the various ingredients, all shades intermediate between deep blue and the palest tones can be obtained.

DARK BLUE (THÉNARD'S BLUE).

Cobalt oxide	80 parts.
Alumina	100 „

The two oxides may be intimately mixed, or else a solution of a cobalt salt is treated with one of aluminium sulphate in suitable proportions, the mixture being precipitated with soda solution and the precipitate washed, dried, and strongly calcined.

COBALT BLUE (PURE DARK BLUE).

Cobalt oxide	60 parts,
Quartz meal	15 „
Refractory stoneware glaze	25 „

are intimately mixed in the mill, strongly calcined, and ground fine.

DARK BLUE.

Cobaltous phosphate	180 parts.
Alumina	100 „

MEDIUM BLUE.

The colour of the above mixture may be progressively lightened by increasing additions of zinc oxide. Ordinary medium blue has the following composition :—

Cobaltous phosphate	34 parts.
Alumina	50 „
Zinc oxide	20 „

PALE BLUE.

Cobaltous phosphate	10 parts.
Alumina	50 „
Zinc oxide	35 „

MIXED BLUES.

These mixed colours can be obtained either by mixing various greens, yellows, or small amounts of black with pure blue, or else prepared direct. Several formulæ are given below, and these, of course, can be modified by altering the proportions, so as to obtain suitable variations in shade.

DARK BLUE-GREEN.

Cobaltic oxide	170 parts.
Chromic oxide	80 „
Alumina	160 „

LIGHT BLUE-GREEN.

Cobaltous chromate	60 parts.
Zinc oxide	40 „
Alumina	100 „

VERY LIGHT BLUE-GREEN.

Cobaltous chromate	30 parts.
Alumina	200 „
Zinc oxide	150 „

LIGHT TURQUOISE.

Cupric phosphate	120 parts.
Tin oxide	150 „

BROWN UNDERGLAZE COLOURS.

These colours are usually prepared from mixtures of manganese oxide, chromic oxide, and zinc oxide, alumina being also used in certain cases.

DARK BROWN.

Alumina	200 parts.
Ferric oxide	80 „
Chromic oxide	76 „

RED-BROWN.

Zinc oxide	194 parts.
Ferric oxide	80 „
Chromic oxide	76 „

LIGHT RED-BROWN.

The same ingredients are used as in the latter case, the proportion of zinc oxide being increased and alumina introduced into the formula.

Zinc oxide	242 parts.
Alumina	51 „
Chromic oxide	76 „
Ferric oxide	80 „

YELLOW-BROWN.

Zinc oxide	325 parts.
Alumina	50 „
Ferric oxide	80 „
Chromic oxide	76 „

MANGANESE BROWN.

Brown underglaze colours can also be obtained by using manganese compounds, the tones, however, differing considerably from those prepared with ferric and chromic oxides. Both very deep and light brown shades can be produced.

True manganese brown consists of a mixture of manganous oxide and alumina, and can be obtained by mixing solutions of manganous sulphate and potassium alum, and treating the mixture with a solution of sodium carbonate so long as a precipitate continues to form, the latter being then washed, dried, and calcined.

Nevertheless, to obtain a given shade of brown, it is necessary to work with definite quantities of materials, the colour depending on the ratio between the manganous oxide and alumina. As an example—

Potassium alum	47 parts,
Manganous sulphate	14 „

are dissolved in water and treated with a solution of 30 parts of anhydrous sodium carbonate.

DARK MANGANESE BROWN.

Manganic oxide	80 parts.
Chromic oxide	75 „

MULBERRY BROWN.

A solution of 14 parts of manganous sulphate is mixed with one of 48 parts of potassium alum (free from iron), and treated with a solution of 30 parts of anhydrous sodium carbonate, the resulting precipitate being well washed with hot water and slightly calcined.

VIOLET MANGANESE BROWN.

Manganous phosphate	178 parts.
Tin oxide	75 „

The mixture is strongly calcined.

GREY UNDERGLAZE COLOURS.

An ordinary grey can be very simply prepared by mixing black with finely ground biscuit sherds in suitable proportions. In order to obtain the same tone in all cases, it is advisable to prepare a colour scale for grey, by mixing the above ingredients in various definite percentage proportions.

PLATINUM GREY.

This grey is prepared by mixing biscuit porcelain meal with platinum-ammonium chloride, and calcining the mass, the platinum compound being decomposed, with deposition of the metal in a very finely divided state, the grey being darker in colour the larger the amount of platinum used.

Platinum-ammonium chloride is prepared by dissolving platinum clippings in a mixture of 3 parts of hydrochloric acid and 1 of nitric acid, carefully evaporating the solution to dryness, and adding to the platinum chloride an equal quantity of sal ammoniac dissolved in water, the whole being evaporated to dryness. The product is dissolved in water and used for uniformly moistening the ground biscuit porcelain, the mass being then dried and gently calcined.

IRIDIUM GREY.

A very handsome grey is obtained by calcining iridium sesqui-oxide with biscuit porcelain meal; but, being more expensive than platinum grey, this colour is rarely used.

BLACK UNDERGLAZE COLOURS.

The simplest method of obtaining a pure black is by using the native mineral, chrome ironstone, which is a compound of ferric and chromic oxides. The selected lumps of the mineral must be free from impurities, and when finely ground, and levigated, are mixed with stoneware glaze or boric acid and treated further.

Various tones of black, brownish, greenish, or blue-black, can be obtained by correspondingly altering the proportions between the ferric oxide and chromic oxide; an addition of cobalt oxide being necessary in the case of blue-black.

BLUE-BLACK.

Ferric oxide	80 parts.
Chromic oxide	76 "
Cobalt oxide	20 "

Of course it is unnecessary for these proportions to be strictly adhered to, and a more decided blue tinge can be imparted by increasing the amount of cobalt oxide, whilst a reduction will give a colour more closely approximating to pure black.

GREENISH BLACK.

Chromic oxide	76 parts.
Ferric oxide	40 "

As with all other mixed blacks, the oxides must be in a very finely divided state and intimately mixed together, the mixture being very strongly calcined (white heat) before use. The high temperature renders all three of the oxides in question more compact and better able to resist solvents. For example, whilst the uncalcined oxides are readily soluble in sulphuric acid, they have to be boiled in the acid a very long time, after calcination, before they can be brought into solution.

BROWNISH BLACK.

Chromic oxide	76 parts.
Ferric oxide	80 „

The brownish tone becomes more and more apparent in proportion as the amount of ferric oxide is increased.

The underglaze colours being usually applied to the unglazed ware, which is very porous, they could not be used mixed with water alone, since the water would be absorbed so rapidly by the ware as to render painting impossible.

To obviate this defect the colours must be incorporated with a small quantity of some substance possessing a certain binding power, so that the colours will stick firmly on the surface of the ware after the solvent has evaporated. Such a medium is found in a very dilute solution of gum arabic or tragacanth, or in concentrated glycerine. The proper amount to be used must be ascertained by trial, since an excess of these organic substances would carbonise and spoil the appearance of the ware when fired.

In the author's experience, however, the best medium for this purpose is rectified oil of turpentine, containing about 1 per cent. of linseed oil that has been boiled to the consistence of syrup. Colours ground with this medium can be applied to the ware with the greatest ease, without being absorbed into the ware. The oil of turpentine quickly evaporates, and the trace of linseed oil is sufficient to cause the colour to stick, without the slightest fear of the decoration being spoiled by the carbonisation of the oil.

In dealing with the methods of decorating ware by mechanical means (printing and transfer papers), we shall see that similar media are employed.

FLOWING UNDERGLAZE COLOURS, OR FLUX COLOURS.

Colours used under glaze must necessarily be of such a nature that they are not attacked by the fusing glaze, or themselves fuse at the temperature of the glazing kiln. The foregoing underglaze colours fulfil this condition perfectly, and will stand the highest temperatures of the porcelain kiln. Nevertheless it can be shown, by the following experiment, that even the pure oxide begins to be volatile, though only to a small extent, at these temperatures.

A design is painted with pure cobalt oxide on a small plate of biscuit porcelain, and over the latter is placed a second plate of the same kind, taking care that they do not touch each other, but have a free space of about $\frac{1}{50}$ th of an inch between them. On exposing these plates to the sharp-fire temperature of the porcelain kiln, it will be found that a replica of the design, in blue outlines, is reproduced on the lower surface of the upper plate. The only way in which this phenomenon can be explained is by the volatilisation of a certain quantity of the cobalt oxide and its deposition on the upper plate.

Stoneware and porcelain are, however, sometimes met with that are painted with cobalt blue designs, the contours of which are not sharp, but soft and pale, as though the colour had been applied wet and had run. The once very popular "onion pattern" ware, made to a large extent in Saxony, formed a very good example of blue flowing underglaze colour.

The chief point in the preparation of these colours is to convert a portion of the oxides present in the colour into chlorides during the firing process. The chlorides of nickel, iron, cobalt, etc., are volatile substances, and begin to volatilise as soon as they are formed, staining the adjacent parts of the glaze deeply, and the more remote portions more and more faintly, until finally the clear white of the glaze appears.

Flowing colours can be prepared in pink, blue, brown, etc., the most frequent, however, being cobalt blue. The glaze used must not be too readily fusible, or it would melt at a temperature insufficient to decompose the chlorides, and therefore would furnish designs of sharp contour instead of in flowing colour.

The volatile chloride generally employed is lead chloride, which is obtained in the form of "flux balls." Since a certain amount of water vapour is always present in the mass, the reaction proceeds on the following lines: the lead chloride and steam form hydrochloric acid when heated, this acid attacking the cobalt compound in the mass and converting it into cobalt chloride which volatilises. This chloride, however, immediately comes in contact with other portions of the glaze, the acid in which breaks it up again into cobalt oxide and hydrochloric acid, the former of which acts as a pigment on this part of the glaze. A small proportion of the cobalt chloride travels somewhat further in the glaze before it meets with the same fate, but as the quantity of cobalt oxide then liberated is small, the colour is fainter; and so on, until, at a certain distance, there are no more vapours of cobalt chloride to come into action, and the glaze therefore retains its original whiteness.

The flux balls, which are placed in the muffle along with the ware, are made in different ways, by mixing lead chloride with various inert substances, and forming the mass into balls about half an inch in diameter. According to one approved recipe, the method of preparing the mass is as follows:—

A mixture is made of 1000 parts of lead acetate, with 100 parts of hydrochloric acid and double that quantity of water, the whole being well stirred and mixed with 1100 parts of dry levigated chalk or finely powdered white marble, and enough water to make the mass up into balls. The latter are dried at ordinary temperature, and are then placed in the

muffles containing the ware to be decorated with flowing colour.

When it is necessary to use glazes richer in lead than usual, the flux balls must not give off vapours of lead chloride until a higher temperature is reached. The mass for these balls is prepared, for instance, of common salt and red lead, with some inert substance such as gypsum, diatomaceous earth, etc. Good results are obtained with a mixture of common salt 6 parts, gypsum 5 parts, and red lead 2 parts; and the mixture may either be made up into balls or placed on a small tray and inserted in the muffle containing the ware.

Of course no other ware may be placed in the same muffle that is being used for flowing colours; and it is better to charge the kiln entirely with muffles so filled, it being very difficult to close the muffles so completely as to prevent the escape of the chloride vapours, for, should the latter find their way into muffles containing ware not intended for this kind of decoration, injurious results would ensue.

As already mentioned, flowing colour decoration is preferably confined to cobalt blues, but other colours can also be treated in the same way. All shades of pink, for example, can be used as flowing colours, no addition being needed when the colour already contains cobalt; and when this is absent, the addition of a very small quantity of cobalt oxide will be sufficient to produce the desired effect.

Underglaze colours containing cupric oxide furnish flowing colours with a greenish tinge. The (brown) nickel colours also need but a very small addition of cobalt oxide to convert them into flowing colours. This circumstance indicates that, at the high temperature, cobalt chloride is first formed, which then reacts on the other metallic oxides to form cupric or nickel chloride exerting a pigmentary action on the adjacent parts of the glaze.

The temperatures at which the underglaze colours are fired

being not immoderately high, the noble metals—gold, silver, and platinum—can be applied under the glaze too. The method of preparing these metals will be described later.

Owing to the difficulty of retouching any defects on ware decorated with underglaze colours, it is usual in the case of artistic ware to first coat the pieces with a refractory white glaze. The colour, mixed with turps and boiled oil, as already described, is then applied to this glaze, from the smooth surface of which any defective portions can be easily wiped off. When the painting is finished, the ware is lightly baked, to destroy the small amount of organic matter present, and is then coated with a fusible glaze. The decoration is thus enclosed between two layers of glaze and thoroughly protected from wear and tear.

CHAPTER V.

APPLYING THE COLOURS ON EARTHENWARE.

AS already mentioned, the best medium for applying under-glaze colours consists of rectified oil of turpentine and a little boiled linseed oil. Provided the amount of medium used be small, the ware can be glazed and fired as soon as the colours are dry; but, especially in the case of fine ware, it is advisable to first bake the pieces lightly, in order to burn off the organic matter which might otherwise spot the colours.

Hand painting, being expensive, is seldom employed except when very fine or very cheap ware is in question. In the former case the work is performed in exactly the same way as in painting on porcelain, and in the other the colours are brushed on roughly, without any attempt at artistic effect. This can easily be seen by examining cheap painted ware.

Of late, however, mechanical appliances have been introduced for painting cheap ware, and furnish much better results than crude handwork. The first of these processes consisted in using stencils arranged so that the parts of the ware not intended to receive colour were protected, the colour adhering only to the exposed parts. A further advance in this direction was the use of elastic stamps and spraying on the colours.

The greatest progress in this direction, however, consisted in the introduction of transfer polychrome printing, which has gradually been developed to such a pitch of perfection that ware decorated in this manner bears so close a resemblance

to hand painting as to deceive the uninitiated. The best proof of the excellence of this method is afforded by the fact that it is now frequently used for the finest porcelain, especially where the reproduction of the same design on a large number of pieces is in question, *e.g.* crests and monograms on table-ware.

APPLYING COLOURS WITH STENCILS.

The oldest method of stencilling is by means of a fine bath sponge, cut so as to present a flat surface on one side. When this surface is applied to the colour spread out on a plate near the worker, the colour will stick to all parts of the sponge brought into contact with it, leaving the pores of the sponge free from colour; and on pressing the charged sponge lightly on the surface of the ware, the colour will be taken up by the latter, the parts corresponding to the pores in the sponge remaining uncoloured.

In this manner a large number of pieces can be coloured in a very short time, and the designs have a very handsome appearance. When flowing colours are used (for which purpose a sponge with rather large pores is best), an intermingled marbling is produced which gives a very fine effect.

The sponging method can be modified in a number of ways, one of them being to cut a spherical piece of sponge and tie it up tightly in a piece of linen, to form a ball, which is fastened on to a handle and dipped in the colour. According to the amount of pressure with which this ball is applied to the surface of the ware, circular patches of colour of different sizes will appear on the ware, a very good effect being obtained with flowing colours.

In stencil work, stencils of various materials may be used, the oldest form being thin sheets of metal (zinc or copper), less frequently oiled paper. The method of using these stencils is simple in the extreme; the operator applies the stencil to the

part to be provided with a given colour, and brushes the fairly dry colour over the exposed surface with a short-haired and fairly soft brush. By this means, and by using a large number of stencils, it is possible to produce certain simple effects. Thus, to stencil a rose, the first stencil plate used is cut to represent the dark red portions of the flower, two lighter tones being put in with a second and third stencil. The green stalk and the leaves can also be reproduced by means of two shades of colours.

THE RUBBER STAMP.

The introduction of rubber stamps constituted a great advance on stencilling, inasmuch as they enable even very fine lines and dots to be transferred in colour, with perfectly clean outlines, to the surface of the ware.

The stamps are prepared by making a model of the inscription or design to be reproduced, in some soft material, which is then used as a matrix, into which the soft, thin paste of caoutchouc is pressed, so as to enter all the finest depressions in the matrix, the rubber being then vulcanised. These vulcanised stamps are very elastic and strong, enabling many thousand impressions to be given without any appreciable wear of the stamp.

Colours to be applied with rubber stamps must be spread, in a thin uniform layer, on an elastic pad. The operator presses the stamp on the pad, thus covering the projecting portions of the stamp with colour, and then applies it gently to the surface of the ware, so as to transfer the colour to the latter. The porous surface of the ware takes up the whole of the colour, and the stamp must therefore be applied to the pad again after each impression.

By using different stamps, each in turn for a separate colour, it is easy to reproduce a number of simple designs, such as flowers, leaves, inscriptions, etc.; and experienced workers

soon acquire sufficient skill in this class of decoration as to produce very handsome effects.

THE SAND BLAST.

Latterly, the sand blast so largely employed in decorating glass ware has found very useful application for coating earthenware with various underglaze colours. The principle of this apparatus is as follows:—

When fine-grained, but very hard, sand is forced against the surface of glass by means of a current of air or steam, working at a pressure of at least several atmospheres, the fine particles of sand exert a remarkably destructive action on the glass. In a very short time the affected parts of the glass become matt, soon after appearing as though engraved, and within a very few minutes a fairly thick sheet of glass will be bored right through by the sand blast.

In the glass industry the sand blast is being more and more used to replace grinding and engraving, the application of suitable stencils enabling any desired pattern to be cut to any depth.

In decorating pottery the sand blast can be used for applying underglaze colours or coloured glazes to the whole or any part of the surface of the unglazed ware.

Similarly, the glaze can be removed from any desired part of the surface of glazed ware, or these portions can be matted in such a way as to enable fresh colour to be applied.

The sand blast is constructed in a number of types, according to the purpose in view, steam being used in some cases to replace compressed air for forcing the sand; but for ceramic purposes the air blast alone is used, though it may occasionally be replaced by the steam blast when glaze is to be removed from parts of the surface of glazed ware.

A sand-blast apparatus, specially suitable for operating on

small articles, and capable of being worked by hand or power, is illustrated in Fig. 16. The vertical cylinder represents the blower, the attached hopper containing the sand, which is

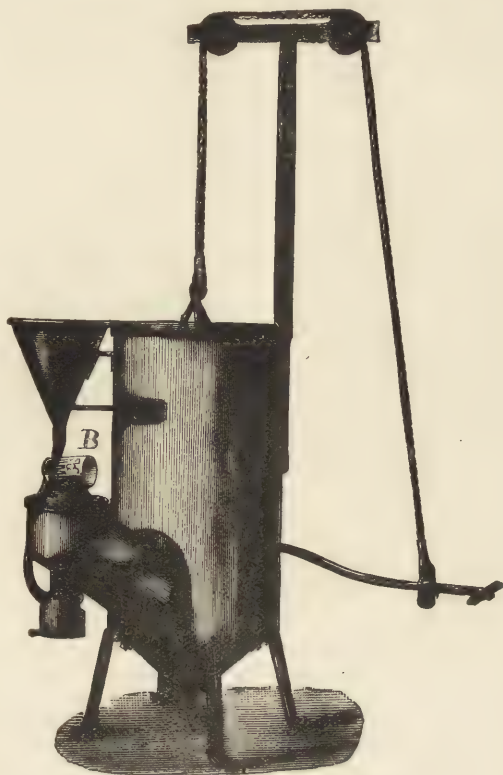


FIG. 16.

carried to the surface of the ware (B) through a rubber tube. With this apparatus it is easy to decorate ware with letters, monograms, or small ornaments.

Figs. 17 and 18 show a sand blast, viewed from the side, and open, in which the pieces can be turned about both on a horizontal and vertical axis, thus enabling the ware to be operated upon in any desired position.

The sand-blast apparatus can be advantageously employed to glaze a large quantity of biscuit ware, the sand being replaced by finely ground glaze and the ware having been previously dipped in an adhesive liquid in order that the glaze may stick. For

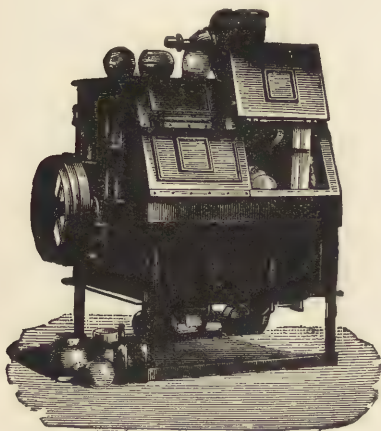


FIG. 17.

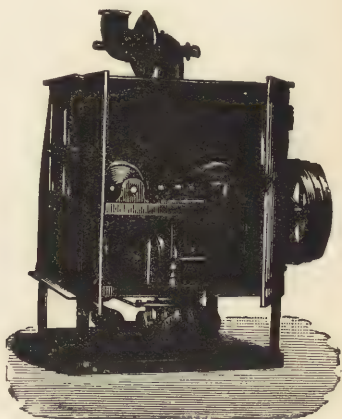


FIG. 18.

this purpose a very weak solution of gum may be used, though suitably diluted glycerine is preferable, this latter substance being strongly adhesive, whilst at the same time it possesses the property of volatilising without residue at a certain temperature. Hence the ware sprayed with glaze can be fired at once.

To apply glaze with the sand-blast machine, the dipped ware is placed in the chamber of the machine, the glaze powder being blown against it as it makes a single revolution on its

axis. The glaze sticks in a perfectly uniform layer and can be transferred to the kiln at once. To enable the work to be performed continuously, the chamber of the machine is divided into two compartments, in one of which glaze is being applied to a piece of ware whilst the other is being emptied and recharged.

By means of this machine, glazes of different colour can be applied to one and the same piece of ware, by protecting parts of the surface during the application of the glazes. Thus, if a more or less cylindrical piece is to appear white in the upper portion and pink below, the lower half is protected by a plate while the top is being sprayed with white glaze, this procedure being then reversed while the lower half is being coated with the pink glaze. Since the protecting plate does not fit absolutely tight against the surface of the ware, there will be no sharp line of demarcation between the white and the pink, but each will blend into the other in a manner very agreeable to the eye.

Designs of all kinds can also be applied in colour in a similar manner, all that is necessary being to cover the piece with a stencil cut out in the parts to be reached by the coloured glaze powder; and in fact, by using a series of stencils, designs of various colours can be reproduced in this machine. As a rule, however, only a single application of glaze is given, polychrome designs being easily reproduced by printing.

For small designs, such as single letters or monograms, in colour on tableware, either a rubber stamp is used, or else the sand blast, the piece in the latter case being covered with a stencil cut to represent the design required.

The most suitable material for stencil plates for coloured glazes is very thin sheet tin or stiff paper, both of which can be applied so close to the surface of the ware as to give sharp edges to the letters, etc., reproduced. Where a large number of reproductions is required it is best to use paper stencils,

a number of which are cut by an iron punch of the proper shape. The stencil being fixed in position against the piece by one workman, a second then holds the piece under the blast nozzle for a moment and passes it on. The work is performed more rapidly in this way than if the one stencil had to be applied to each piece.

To remove the glaze from any particular part of a piece of glazed ware, a sand blast must be used, by means of which sharp quartz sand is impelled against the place with considerable force. This soon removes the hard but thin coating of glaze, and reveals the matt surface of the biscuit.

This method can be advantageously adopted for decorating large pieces of art ware, such as vases, etc., with gold or colours. The vase is completely covered with colourless glaze, and over this is applied a thick paper stencil, cut away in the parts where the glaze is to be removed from the vase, *e.g.*, an oval surface on which a picture is to be painted. The vase is then put under the sand blast, the removal of the glaze being indicated by the appearance of the matt surface of the biscuit. The surface can then be gilded or painted in any desired way, the colours being finally fired in the muffle. The sand blast may also be used for rectifying defects, such as specks, dots, unevenly flowed patches, etc., in the glaze of expensive and otherwise perfect pieces, the matted surfaces being afterwards reglazed.

APPLICATION OF COLOURS TO THE WARE BY TRANSFERS.

The so-called "printing" on stoneware and other ceramic bodies is not really printing in the ordinary sense, but a transference of a printed impression. Since polychrome designs can be applied in this way as well as those in monochrome, the process enjoys widespread application in ceramics, especially since it reached its present state of perfection, because it has solved the problem of decorating ware in a cheap and simple manner with very handsome designs.

The essential feature of the transfer process for ceramic purposes consists in making an impression on specially prepared paper of a design engraved or etched on a plate of steel, copper, or stone (aluminium also of late), ceramic colours of course being used. The fresh impression is applied to that part of the ware which is to be decorated, and is pressed firmly thereon. The adhesive colour sticks very fast to the porous ware, and the specially prepared paper can be carefully peeled off, leaving the design behind. The ware is then exposed to a low red heat, to destroy the binding medium with which the colours have been ground, after which it is glazed and fired.

Although the entire method of the transfer process has been sketched in these few words, a great number of precautions are needed in its performance, since it is only by observing these that really perfect transfer pictures can be produced on ceramic ware.

THE ORIGINAL PLATES FOR TRANSFER PRINTING.

At one time steel or copper plates were used exclusively, the latter being preferred on account of greater ease in production and the softness of the contours. Latterly aluminium plates have been largely used, this method of reproduction, known as "algraphy," being more frequently employed than litho work.

TRANSFER PRINTING FROM STEEL OR COPPER PLATES.

Whatever the kind of plate used, the engraving or etching must be unusually deep, since a very thick, viscid varnish is used for printing. At one time the production of the printing plates was an expensive matter, the soft copper plates soon wearing away and needing to be recut. At present, however, this defect has been remedied, the original plate being no longer used for printing, but only as a matrix for making a large number of electros.

In the first place, a plaster or gutta-percha cast is taken from

the original plate, and after rubbing the cast over with finely levigated graphite to render it conductive, an electro is prepared which reproduces with perfect fidelity all the features of the original plate. In the case of a design that is to be used for a very large number of pieces, and is therefore liable to wear away quickly, a large number of these electros are made, so that as soon as one shows signs of wear it can be discarded and replaced by a fresh one.

Since the electros are of chemically pure copper, which is of a very low degree of hardness and would very soon wear down, they are usually faced with cobalt or steel, the very thin layer of the harder metal deposited on the copper having no injurious effect on the sharpness of the impressions.

The best way of facing the plates with cobalt is by dissolving 40 parts of cobalt chloride, 20 parts of sal ammoniac, and 20 parts of ammonia in 100 parts of water, in the order given. When a plate of clean copper is dipped in this solution and connected with one of the poles of a battery, a very feeble current is sufficient to quickly cover the surface of the copper with an extremely thin film of metallic cobalt, the plate having the appearance of silver.

The so-called steel facing of the copper plates is really iron-plating, as the deposition film consists of iron and hydrogen, free from any trace of carbon (the characteristic ingredient of steel). The plating, however, is as hard as the hardest steel—hence its name.

The easiest way of iron-plating copper is that recommended by Professor Meidinger, which is performed in the following manner:—

Two parts of ferrous sulphate and 1 of sal ammoniac are placed in an air-tight bottle, followed by 1 part of soft, rust-free iron (small shoe brads) and sufficient water to dissolve the salts, the whole being then left for several days. The metallic iron serves the purpose of preventing the conversion of the ferrous oxide into the ferric state. The plating process is

carried on in a wooden or glass trough, which is deeper than the length of the copper plate, but only about 2 inches wide. The copper plate is placed against one wall of the trough, with an iron plate in a parallel position against the other wall, and the trough is filled with the liquid mentioned above. The two plates should not be more than $\frac{5}{8}$ th inch apart; and the copper plate is connected with the negative pole of a battery, whilst the iron plate is connected to the positive pole. The deposition of the iron begins at once, and the film of metal will attain the desired thickness in 5 to 15 minutes. The plate is then taken out of the trough, rinsed with a large quantity of water, followed by washing in a solution of sodium carbonate, and finally by rinsing in water again, after which it is dried. When properly coated, the plate has a shiny, handsome grey appearance.

The copper plate must be made perfectly bright before immersion in the plating bath, by dipping it in caustic soda lye for a few minutes, rinsing it in water, then dipping it in very dilute sulphuric acid, followed by a thorough rinsing with water; after which it is placed, wet, in the bath.

PRINTING ON THE TRANSFER PAPER.

The transfer paper for receiving the impression from the engraved plate is prepared in a special manner, and must be of such a nature that the paper can be drawn away from the baked ware at a certain stage of the transfer process, leaving the coloured print adhering to the ware.

The transfer paper must be as thin as possible, whilst at the same time possessing considerable strength. These two properties, which are difficult to combine, are most readily found in carefully made hemp paper. Other fine papers, however, can be used, the chief essential being that the paper is of long staple, and subjected to heavy pressure in the finishing process.

Before use the transfer paper must be coated with soap on the

side to be printed, so that the colour does not come into direct contact with the paper, but rests on the layer of soap.

The soap mass for this purpose is prepared by cutting good white curd soap into fine shreds, and boiling these with pure water in a vessel until fully dissolved, so as to form an opalescent but transparent liquid that is viscid when warm, and in this condition will flow from the spatula. The presence of dark patches in the mass indicates that some of the shreds, though swollen, are not dissolved. The soap solution must be spread evenly over the paper.

This operation can be performed by hand, but requires much practice to ensure uniform distribution. The best way is to brush it over the paper with a broad soft brush in parallel strokes, and then work the brush in a direction at right angles with the first. Where large quantities have to be coated it is preferable to use a small machine, consisting in the main of a rubber-faced roller, mounted underneath the vessel containing the soap solution. The latter flows in a stream the full width of the roller, and is distributed evenly over the surface of same by means of a doctor. The paper to be coated is drawn gently under the roller, and exhibits a uniform coating after a single passage through the machine.

The preparation of the printing colours also differs from that of colours for ordinary copper-plate printing. The colours used are underglaze colours in the highest possible condition of fineness. These colours are ground along with a very thick copper-plate varnish in roller mills, such as are used in making ink for the finest art printing.

The resulting colours are far too thick to be fit for use at ordinary temperature, but since they become much thinner when warm, this property is utilised to enable them to distribute properly. As a rule, the printing colour is placed on a polished cast-iron plate, mounted horizontally on a suitable frame, and warmed from below, preferably with a

small gas flame, the colour spread on the plate being rubbed down with the necessary quantity of thick varnish.

The copper printing plate is also strongly warmed, and while in this state is inked with the colour, by means of a wooden spatula, with which a quantity of the colour is taken out from the plate and spread over the copper plate gradually until the whole surface of the latter is covered. The spatula is drawn over the plate in various directions to make sure that the viscid colour has filled up all the depressions in the deeply engraved plate. This done, the copper plate is laid on a table and the surplus colour is removed with the palette knife, a very thin but broad blade of highly flexible steel. The knife is applied to one of the narrow sides of the copper plate and then drawn evenly over the entire surface, the operation being repeated until barely any colour is visible.

The final traces of the colour are removed by means of a pad of soft leather stuffed with soft calves' hair. After being energetically rubbed over with this pad, the plate is cleaned once or twice with a second pad of soft material.

The plate is now ready for printing, for which purpose it is laid on the bed of the press and covered with the paper, coated side downward, the paper being backed with a damp linen cloth covered with a layer of felt, and the whole being spread out quite smooth. The upper roller of the press must also be faced with felt, in order that the pressure may be distributed uniformly all over the paper. The plate is run to and fro through the press, and the paper then taken out.

For coloured prints the paper is treated in exactly the same way as in ordinary colour printing, the several colours being printed in succession just as with oil colours. The designs to be applied to the ware being generally very small, an endeavour is made to utilise the surface of the printing plate as much as possible, in order to obtain a maximum number of designs on the sheet.

After the impression, the printing plate and paper are laid on a level metal plate, uniformly warmed from below by means of a number of small gas jets, or else with a hot-water jacket, kept at boiling temperature by gas flames, so that the top plate is raised to a uniform temperature of 100° C. all over.

The plate and paper are left in this position until the latter is perfectly dry and can be lifted from the plate without pulling. The paper is then turned printed side up, and all the unprinted portion is cut away, as closely as possible, with scissors.

TRANSFERRING THE DESIGN.

The transference of the design to the baked ware is effected by applying the printed side of the paper to the parts on which the design is to appear, and pressing them down smoothly with the hand. When the paper lies quite evenly on the ware, it is pressed with a rubbing tool, consisting of a wooden rod covered with soft thick flannel, surrounded by an evenly wound layer of string. To enable the rubber to be moved smoothly over the paper, it is rubbed well on a cake of hard soap.

The paper is pressed evenly on the ware with this tool, which is then applied several times in succession under strong pressure and a drawing motion. The ware is next placed in a vessel containing water at a temperature of about $30-40^{\circ}$ C., in which it is left until the paper is seen to be peeling off. This contact with warm water causes the paper to swell up rapidly, and the intermediate layer of soap dissolves, thus destroying the connection between the paper and the colour. All that is then necessary to detach the paper completely, is to move the ware about in the water several times. On no account should an attempt be made to hasten the separation of the paper by pulling it, because it only sticks

at the points where the soap has not yet properly dissolved, and consequently portions of the colour would be pulled off along with the paper, and the design would be spoiled.

The design is now on the ware, but is not yet ready to be fired or glazed, owing to the presence of the printing varnish, which would be carbonised by the heat, its vaporous decomposition products at the same time producing bubbles in the glaze, and the carbonised residue making the design unrecognisable. For this reason the ware must be first exposed to a temperature equivalent to dull red heat, to destroy the varnish and leave only the colour on the surface of the clay. This operation must be performed in muffles, of such dimensions as to accommodate the largest possible number of pieces in each.

When red heat is attained, the ware is left in the muffle to cool down to the ordinary temperature again, after which it is glazed and fired. To prevent any chemical reaction between the colours and the glaze, the latter should be readily fusible, and the glazing temperature no higher than necessary to make the glaze flow properly.

TRANSFERS FROM LITHOGRAPHIC PLATES.

When transfers are printed from plates of metal, whether steel or copper, only monochrome designs can be reproduced, and these merely in outline or with stippled shading. By means of lithography, however, it is possible to reproduce designs in any number of colours, by transfers, so that the finished ware looks as though painted by hand. Analogous results can also be obtained by the newer process of algraphy (printing from aluminium plates) and by the collodion process.

¶ In litho work the design is either drawn on the stone with black litho chalk, or else painted with lithographic inks, both media having the property of resisting the liquid (generally

very dilute nitric acid) used for etching the stone, whilst they are easily removed from the stone afterwards.

After drawing, etching, and cleaning the stone, the design appears on the surface of the latter in relief, and will take up colour from an inking roller, leaving the depressions blank. On applying suitable paper to the inked stone and putting both through the press, the colour is taken up by the paper, leaving the stone to be re-inked for a fresh impression.

For multiple colour printing—chromo-lithography—the so-called transfer process is employed. By means of transfer ink as many impressions are taken from the original plate as there are colours in the design, and these pulls are transferred to other stones, one stone for each colour. The next step is to obliterate from each stone all the transfer ink except in the places corresponding to the colour to be printed by that stone; and when all the stones have been treated in this way, printing may commence.

It follows, as a matter of course, that precautions must be adopted to make the sheets of paper register properly on each stone, so that the colours shall be printed in exactly the places where they belong. This is effected in a very simple manner by marking the first plate with two lightly drawn crosses near two corners. These crosses will then appear on each pull and on each stone, and, a small hole being bored into the paper and the stones at the points of intersection of the cross lines, the sheets of paper are fixed in position by means of pins.

In making colour prints for transfer to ceramic ware, the colours must be of a suitable character and ground with the printing varnish: and very good printing paper must be used, this being first coated with an intermediate layer of material separating the colour from the paper—as already described under printing from copper plates—so that the paper can be removed after the transfer has been applied to the ware. The materials used for this intermediate layer must

be capable of either dissolving easily in water or of swelling up quickly in that liquid. Hence, use may be made of solutions of gum, glue, or dextrin, which are soluble ; or else of starch paste or tragacanth, which swell up quickly in contact with water, and therefore are also readily detached from the layer of colour. These solutions may be employed separately or mixed.

To enable this intermediate layer to be uniformly distributed over the surface of the paper without difficulty, it is advisable to stain with a little fuchsin or other coal-tar dye. The coating of adhesive material is then applied by means of an inking roller.

The printing process is the same as described for copper plates, but the varnish need not be so strong as in the latter case.

COLOUR PRINTING.

The operations of colour printing are the same as practised by the lithographer with ordinary inks. One colour is printed at a time, and the sheets coming from the press are laid aside until the whole impression is run off, whereupon the next colour is printed, and so on, until the design is completed. The only difference between this process and ordinary printing is that the colours are printed in reverse order, those intended for the background being printed last, so that when the transfer is applied on the ware the series will appear in proper order.

Another method is to print from each stone in varnish only, and then dust the corresponding colour over the paper, to which it will adhere only in the parts covered with varnish, the surplus colour being removed by blowing. In this case, of course, the paper must be left long enough after each application for the varnish to dry thoroughly before printing the varnish for the next colour.

The transference of the design from the paper to the porcelain is effected in the following manner :—

All the unprinted portions of the paper are cut away with the scissors as carefully as possible. The paper is then laid, printed side downward, on a smooth sheet of blotting-paper, and moistened on the back with a sponge just sufficiently for the water to penetrate through the paper and cause the intermediate layer to swell, but without wetting the printed side.

The parts of the porcelain ware to be decorated are painted over with a very dilute lacquer varnish, which is left to dry until very tacky. The transfer is now applied to the ware, and pressed on the same, from the centre outward to prevent air-bubbles, any small bubbles that cannot be helped being pricked with a needle and the air forced out by careful pressure with the fingers, followed by rubbing the paper smooth.

This done, strong pressure is applied, and the ware is placed in water. After a short time the paper will detach itself from the ware, in consequence of the intermediate layer having become dissolved. The ware is then taken out of the water and left to become perfectly dry in a place free from dust. The next step is to examine the ware and remedy any defects in the design by hand. Additional colours can also be applied ; this being frequently the case with gold, to avoid the risk of loss of the metal in transfer printing.

The transfer process is greatly facilitated by the use of collodion paper instead of papers coated with gum or the like. This paper can be prepared by coating dried gummed paper with a layer of elastic collodion, obtained by mixing 100 parts of commercial collodion (which usually contains 4 per cent. of gun-cotton) with an equal quantity of very strong alcohol, together with 4 parts of castor-oil and 8 parts of Canada balsam, a small quantity of coal-tar dye being added to make the collodion visible when applied to the paper. The colours are then printed on the collodion in the usual way.

The transfer is accomplished as follows :—

The paper is immersed in water, which soon loosens the layer of collodion carrying the colour. As soon as this separation is observed, the paper is applied to the ware, and can then be easily drawn away from the collodion layer, leaving the latter and the colour adhering to the ware. This process offers the twofold advantage of enabling the paper to be detached without risk of tearing, whilst, on the other hand, the colours can be readily seen through the transparent collodion, so that it is easy to apply the transfer exactly at the spot the design ought to occupy on the ware. In the subsequent operation of burning in the colours, the collodion film burns away without any residue.

The collodion process is also suitable for gold printing, the parts to be gilded being printed over with a mixture of ferric oxide, bismuth oxide, and lampblack, and the gold leaf applied as in gilding. The surplus gold is wiped off after the varnish is perfectly dry.

ALUMINIUM PRINTING (ALGRAPHY).

Recently a convenient modification of lithography has been adopted, consisting in the employment of aluminium plates, instead of stone, for multiple colour printing. This method, which is known as "algraphy," has the advantage that the aluminium plates are very thin and are no heavier than glass plates of the same thickness, whereas litho stones are very thick and heavy, and are easily cracked in the press if carelessly handled, a defect to which aluminium plates are not liable.

The preparation of the aluminium plates is similar in many respects to that of litho stones, and the design is drawn on the plates in the same manner. The etching process, however, is different, a solution of ordinary (ortho-) phosphoric acid being used. The etching bath is prepared by making a solution of

phosphoric acid, of exactly 20 per cent. strength, and a 10 per cent. aqueous solution of gum arabic, the two being mixed in the proportion of 10 parts of gum solution to 1 of acid solution. The etching liquor may be poured on the surface of the plate, but is usually applied by means of a small bath sponge, with which the plate is damped, so as to avoid bringing any great excess of the liquid on the plate.

The time occupied in etching depends on the depth to which the plate is to be bitten, fairly deep etching being required for plates for ceramic transfers. The etched plate is rinsed with a large quantity of water, and the chalk or lithographic ink is then removed.

In order to protect the original plates from wear they are used solely for making copper electros, these alone being used for the printing, whilst the originals are carefully preserved.

DECORATING PORCELAIN BY PHOTOGRAPHY (PHOTO-CERAMICS).

The transfer of photographs to ceramic ware is an art usually confined to porcelain, although it could be extended to other ware. The chief reason for its restriction to porcelain is that the art itself constitutes the highest stage of ceramic decoration, whilst porcelain is the finest product of the ceramic industry.

The reason for dealing with the photo-ceramic art in this place, along with methods of decorating earthenware in colour by mechanical means, is because it belongs properly to this class of operations, and rounds off the series. The decoration of porcelain with stencil work and transfer printing is essentially performed in the same way as in the case of earthenware; and therefore, to complete the description of mechanical decoration and avoid repetition, the author has thought it advisable to describe the photo-ceramic process now, though this is usually confined to porcelain ware. The process is fully

described in special works on the subject, dealing with the purely photographic side of the matter, which cannot be entered into here, our object being merely to treat of the application and fixation of the photographic pictures to the ware.

Portraits, landscapes, and all other descriptions of photographs can be applied to porcelain with the absolute sharpness and fine detail of the best photographic pictures. Porcelain being unaffected in the slightest degree by atmospheric influences, or even very severe fluctuations of temperature, and only destroyed by mechanical forces, the photo-ceramic process affords a means of reproducing important pictures, such as portraits of celebrities, rare natural objects, etc., in a manner beyond the possibilities of any other process, these pictures being almost indestructible, and capable of retaining their pristine appearance for centuries unless forcibly broken.

The production of photographic pictures being a matter chiefly concerning the professional photographer, we cannot go closely into detail on the purely photographic side of the same, but must chiefly confine ourselves to the operations intimately relating to the transfer of the picture to the ware.

In taking a photograph, a portrait for instance, by the dry plate process a negative is first obtained, in which the white portions of the original subject are dark, and *vice versa*, the white face being black in the negative and the dark clothes light. If such a negative were transferred to porcelain, a negative picture would be obtained, and it is therefore necessary to make a positive picture first.

This is done in a very simple manner by placing a sensitive plate behind the negative in a printing frame in a dark room, and then exposing the two to the light. This furnishes a positive picture, in which the distribution of light and shade is the same as in the original subject at the moment the picture

was taken. Whether the positive is made on a sensitive collodion film or on a plate prepared in some other way, depends on the special process employed in producing the ceramic picture.

When collodion plates are used, the finished collodion picture must be detached from the glass support whilst still wet—an operation entailing considerable skill by reason of the extreme thinness and low tensile strength of the collodion film. The easiest way is to raise the film at one corner of the plate with a very thin knife blade, attach it to a glass rod and carefully turn the latter round and round so as to draw the film from the plate and wrap it round the rod. The latter is then held over a shallow dish containing water, and turned in the opposite direction until the whole of the film has unrolled and lies as a thin coherent pellicle in the water. After being washed repeatedly with distilled water in this dish, the film is strengthened.

Stripping the film in the first place is facilitated by the following artifice:—The sheet of glass for supporting the positive is first coated with a film of unsensitised collodion, and just as this is beginning to set, the coating of sensitised collodion is applied. This gives a much thicker film, which can be detached from the glass without risk of tearing.

The image on the collodion film consists of finely divided silver, a greater quantity of the microscopic silver crystals being present in the dark parts than in the lighter places. Attempts to transfer this image to porcelain would be unsuccessful, the amount of silver present being on the one hand too small, and on the other being attacked by the glaze. It is therefore essential to convert the silver image into an image composed of a metal that is not attacked by the glaze in the firing process.

This transformation can be effected in various ways; but whatever metal be used it must be employed in the state of a

chlorine compound. Thus, when the film carrying the grey silver image is immersed in a dilute solution of gold chloride or platinum chloride, the colour of the image will soon be observed to change to a reddish brown, in the case of gold, or steel grey in the case of platinum. The reaction occurring consists in the silver combining with the chlorine in the solution and causing the deposition of finely divided gold or platinum.

When the image has been "toned," as the photographer terms it, in this way, the film must be fixed in a bath of sodium hyposulphite (thiosulphate) in order to eliminate the silver chloride.

The best toning agent for pictures for ceramic purposes, in addition to platinum chloride, is iridium chloride, which gives a deep black image. Mixtures of platinum chloride and uranium chloride furnish handsome warm reddish-brown tones when fired. A manganese chloride toning bath gives a warm brown tone, similar to sepia paintings. The tone may be modified by an admixture of ferric chloride with manganese chloride or uranium chloride, so that pictures of various colours may be reproduced on the ware.

The toned picture is then laid face downward on the ware, and after being smoothed down perfectly level is dusted over with the flux necessary for the firing process. The flux may also be applied, in the form of a thin wash, by means of a soft brush. When both picture and glaze are perfectly dry, the ware can be fired.

The collodion process is often replaced by a dusting process, based on the fact that a mixture of dissolved gelatine and potassium bichromate in suitable proportions forms a mass that is sensitive to light. If a glass plate be coated with this mixture in the dark room and allowed to dry, a sensitive plate is obtained that can be exposed under a negative. The parts of the gelatine-bichromate to which the light penetrates through

the negative are rendered insoluble, whilst the protected parts remain soluble.

The whole plate is next dusted over quite evenly with porcelain colour in an extremely fine state of division, any surplus being removed by blowing with a small bellows (not with the mouth, on account of the water vapour always present in the breath).

As already mentioned, the gelatine is rendered insoluble in the parts affected by light, and therefore no colour will adhere to that part; whereas the unexposed portions remain soluble and tacky, and take up the colour so that the photographic picture appears on the gelatine plate as soon as the colour is dusted on.

When the surplus colour has been blown away, the loosely adhering powder must be fixed by pouring over it a layer of collodion, rendered supple by an admixture of castor-oil, thus imprisoning the colour between the collodion and the gelatine. When the collodion is thoroughly dry, the edges of the picture are cut round with a sharp knife, and the plate is laid in water, in which the soluble parts of the gelatine dissolve. After being washed, the film is applied to the ware, the collodion film being underneath. The subsequent operations applying the flux and firing the ware are the same as for the collodion process.

Porcelain ware decorated by the photo-ceramic process is not made in large quantities at a time, but generally in single pieces, such as cups, small vases, etc., that have to be decorated with some picture. For this reason the pieces are fired in small muffles, heated with wood charcoal, or preferably with coal-gas, and not in the large muffles used for hand-painted ware.

As a rule the method of firing differs but slightly from that of painted porcelain, and therefore need not be dealt with until we come to describe the process of firing the ware in large muffles,

DECORATING PORCELAIN WITH COLOURS, METALS, AND LUSTRES.

Porcelain, as the highest product of the ceramic industry, is excellently adapted, by reason of its beautiful pure white colour, for being decorated with colours and noble metals, the more so because a whole series of processes can be employed for the accomplishment of this purpose. The colours may be applied either before or after glazing, and by hand-painting as well as by transfer printing or photography.

In addition to painting with ordinary colours, porcelain ware may be specially decorated in several ways, namely, by means of the three noble metals, gold, silver and platinum, or by a special treatment for the purpose of producing a metallic lustre or iridescence. In a word, the decoration of ceramic articles with colours and metals has reached its highest stage in the case of porcelain; and numerous articles of this class occupy the first rank as works of art. Moreover, owing to the great progress made, it is now possible to produce, by mechanical means and at a correspondingly low price, very handsome specimens of porcelain that closely resemble hand-painted ware.

CHAPTER VI.

GLOST FIRE COLOURS.

THE colours employed for decorating porcelain may be divided into two classes: those applied to the biscuit ware previous to glazing, and therefore corresponding to the "underglaze colours" for earthenware, though generally termed "glost fire" colours in the case of porcelain; and those applied over the glaze, and known as "muffle" colours, since they have to be fired in muffles in order to secure their fixation on the ware.

A further distinction is drawn, in the case of porcelain, between glost fire colours applied before glazing, and glost fire colours in general. Those in the former category are not often used, most porcelain being decorated with colours after the ware has been glazed. In this case the name glost fire colours is justified, inasmuch as the temperature of the kiln must be hot enough to soften the glaze again and enable the colours to sink in.

Not many pigmentary substances will stand this heat without undergoing volatilisation or change. The three chief substances fulfilling these requirements are cobalt oxide, chromic oxide, and iron oxide. The "onion" pattern first introduced by Saxon porcelain manufacturers and very popular at one time was produced by means of cobalt blue.

These colours are applied by mixing them with water containing enough binding medium, such as glycerine or gum

water, to render the mass workable with the brush. In the case of very porous ware, however, these means are insufficient, and recourse has to be had to oil of turpentine ("thickened oil") that has been left to stand in partly filled bottles until viscous.

Since the underglaze colours are rarely employed more than one at a time, they can be applied to the ware by means of stencils or transfer printing, hand-painting being rarely used.

GLOST FIRE COLOURS OVER GLAZE.

The application of these colours to glazed ware is a less difficult matter than to biscuit, the glazed ware being no longer porous and therefore not absorbing the colour. However, to ensure the colour sticking to the surface, the former must be ground along with thickened oil, though the quantity of this latter should be kept at the minimum.

After the colour has been applied, the ware must in all cases be left for some time before proceeding to the firing stage, in order to allow the oil of turpentine to evaporate completely and the thickened oil to resinify. In the kiln the ware must naturally be heated to a temperature sufficient to resoften the glaze to such an extent that the colour will sink into and become incorporated with it. The designs produced in this way exhibit a high degree of softness, the contours losing their sharpness.

In many cases an attempt is made to avoid these high temperatures by mixing with the glost fire colour a small quantity of a similar colour of lower fusing-point, the finished painting being coated with a readily fusible glaze. Both the added colour and the overlying glaze must have such a low fusing-point as to melt completely at the temperature of the ordinary muffle.

The decorated ware is fired in the muffle, thus embedding

the painting between two layers of glaze. Apart from the low cost of fuel in this method of firing, there is the additional advantage that the colours remain unaltered, which will not be the case if any reducing atmosphere gains access to the ware in course of firing in the ordinary kiln.

CHAPTER VII.

MUFFLE COLOURS.

ALL the colours that are fired on ceramic ware in closed chambers of special construction, termed "muffles," are known as "muffle colours." Both these colours and the fluxes with which they are used must have a relative low fusing-point, the firing temperature being a low red heat. For this reason the most delicate colours can be used in this branch of porcelain painting, and hence the painter is offered a wider range of colours than in any other method.

In the majority of muffle colours the actual colouring matters are not themselves fused; and in some cases use is made of colours capable of standing the greatest heat; but the flux, or fusible glass, with which the colour is intimately mixed, fuses and envelops the extremely fine particles of embedded colour.

FLUXES AND THEIR COMPOSITION.

As stated above, the fluxes consist of readily fusible glasses, which melt in the muffle and envelop the colouring matter. The glasses used are those of the fusible lead group, frequently containing boric acid, in addition to silica, for the purpose of increasing their fusibility. Apart from the alkalis necessarily present in the fluxes, an admixture of bismuth oxide is given in certain special cases.

It would be highly convenient to be able to use one and the same flux for all the colours employed in porcelain painting; but this is impossible on account of the injurious action of

some of the ingredients of the fluxes on certain colours, the colour of the finished ware then turning out different from the shade desired. Hence, to prevent this defect, certain definite fluxes must be used with certain groups of colours.

The porcelain colours capable of standing a high firing temperature can be mixed with refractory flux. To this class of colours belong the blue cobalt colours and most of the iron red colours, the pure chrome greens also being able to stand refractory fluxes.

The case is, however, different with the colours ranging from pink to dark purple red and usually obtained by the aid of gold-ruby or copper-ruby glass. These colours will not stand any high temperature without their beauty being considerably impaired, and therefore must be mixed with fusible fluxes, prepared by modifying the composition so that a large part of the silica is replaced by boric acid. The fusing-point of the lead borate glasses is fairly low, and by this means the most delicate tints obtainable with ruby glass can be preserved in all their purity.

The composition of the fluxes generally used differs in different works, but in most cases approximates to the following formula :—

ORDINARY (GREY) LEAD FLUX.

Red lead	75-80 parts.
Quartz sand	25-20 „

This flux, which in composition is a pure lead silicate, may be used with the blue cobalt colours and for certain reds produced by means of ferric oxide.

The flux is made either as a lead glass, containing boric acid in addition to silica, or else in the form of a lead-soda glass in which a portion of the silica is replaced by soda.

I. Quartz sand	23 parts.
Red lead	66 „
Borax (anhydrous)	11 „

II. Quartz sand	16 parts.
Red lead	61 „
Boric acid	23 „

This grey flux can be used for a large number of colours, and especially for the yellow, pale brown, and red iron colours, as well as for grey tones.

GREEN FLUX.

Quartz sand	70-73 parts.
Red lead	10-18 „
Boric acid	20-9 „

This flux can be used both with pure chrome green and for the various mixtures of blue and yellow, mostly compounded of chromic oxide, cobalt oxide, and pure yellow.

For very delicate water green and very pale bottle green, as well as pure turquoise blue, use must be made of a flux that is highly fusible, generally pure lead borate without any silica at all. The composition of this lead borate corresponds to the following formula:—

Red lead	35 parts.
Boric acid	65 „

It should be noted that this lead borate is very susceptible to the action of acids, the decoration on porcelain painted with colours of this kind being quickly destroyed by contact with strong acids.

FLUXES FOR CARMINE RED.

There are several different formulæ for carmine fluxes, some of them being suitable for very delicate pink and light purple, whilst others are better adapted for use with dark purple red.

FLUX FOR CARMINE AND LIGHT PURPLE.

Quartz sand	34 parts.
Red lead	12 „
Borax	58 „

FLUX FOR MIXED DARK PURPLE.

Quartz sand	15 parts.
Red lead	38 "
Boric acid	50 "

FLUX FOR VIOLET.

Quartz sand	5 parts.
Red lead	68 "
Boric acid	28 "

PREPARING THE FLUX.

In the main the preparation of fluxes follows the same lines as that of the fine glazes. Operations are commenced by reducing the various ingredients to very fine powder. Care must, however, be taken to avoid using any appliances containing metal, since even the finest metallic particles that might gain admittance to the fluxes could impart coloration thereto. Hence the selected fragments or quartz (which must be perfectly free from iron) are first ground in an edge-runner mill, and then in ball mills lined with quartz or porcelain, the reduction of the mass to powder being effected by the aid of round lumps of quartz.

The ingredients must also be mixed together with the greatest care, since, if not effected with the necessary intimacy, the composition of the mass will fluctuate when fused, and its chemical and physical properties will vary accordingly.

Red lead being a specifically heavier body than the other ingredients of the flux, will tend, if imperfectly mixed, to form a glass very rich in lead at the bottom of the melting vessel, leaving the upper layers progressively poorer in lead; and this difference will not be entirely compensated during the subsequent grinding of the mass.

To prevent the evils arising from this cause it is advisable to

raise the empty crucible to a strong red heat before introducing the charge of flux materials, the latter being also heated nearly to redness beforehand, and quickly placed in the crucible, the fire being then made up strongly. In these circumstances the mass melts in a very short time to a glass of very uniform composition.

The operation of melting is performed in crucibles arranged in the same manner as already described in the preparation of glazes. Owing to the rapidity with which these masses melt, when treated as above, it is advisable to use crucibles in which the bottom valve can be lifted by a rod. As soon as the charge is found to be melted—and with a little experience the time can be forecasted to within a few minutes—the valve is lifted and the thin glass allowed to run out. When the flow ceases, the valve is shut and the crucible recharged with heated material.

To rapidly cool the molten flux and at the same time make it very brittle, thus facilitating the subsequent grinding process, it is run out of the crucible into a vessel of water, in which it sets to colourless masses. This treatment cannot, however, be applied to fluxes rich in boric acid, since the water, which soon becomes boiling hot from contact with the glowing mass, would have a powerfully decomposing action on these borax glasses.

This defect can be obviated by replacing the vessel of water by an inclined smooth iron plate, in front of which is arranged an iron trough. The fluid glass escaping from the crucible when the valve is opened, falls down the iron plate into the trough, where it is sprinkled with a fine spray of water until it sets. As the water is evaporated immediately, there is no risk of its attacking the glass.

Properly made flux is a perfectly colourless glass, with a high index of refraction and high specific gravity, and generally exhibiting all the characteristics of the true lead glasses.

The molten and recooled mass has next to be reduced to fine powder, in which operation care is again necessary to prevent contamination with metallic particles.

At this stage the preparation of the colours for painting on porcelain can be proceeded with, the work consisting in mixing the powdered flux with the colour in definite proportions, the whole being performed in such a way as to furnish a number of shades of the same colour. The larger the proportion of flux in comparison with that of the pure colour, the lighter the resulting shade. In making up a colour for the first time it is essential to work on a definite plan, so as to obtain a reliable guidance for subsequent operations. The best method of procedure is the following:—

A mixture is prepared containing 90 parts of the pure colouring matter to 10 parts of flux, this mixture being marked No. 1. A second mixture contains 80 parts of colour and 20 of flux, and is marked No. 2. The third mixture (No. 3) contains 70 parts of colour and 30 of flux, and so on, until No. 9 mixture is prepared, consisting of 10 parts of colour and 90 of flux.

A flat porcelain tile is painted over with strips of each colour, the strips being numbered accordingly, and fired in the usual manner. We then have a specimen of each of the nine shades on the one tile, and any of these shades can be matched at any time by taking the proper proportions of flux and colour.

These specimen tiles are very important for the painter on porcelain, enabling him to find at once the exact shade he wants. In the event of the required shade being intermediate between any two of the regular Nos., it can be easily obtained by taking the next darker number and reducing it with a little flux.

So far as the muffle colours are concerned, a number of the substances used in their preparation are identical with those for glost kiln colours, cobalt being the pigmentary

principle for blue in both cases, chrome for green, manganese for violet, etc.

Owing, however, to the lower temperature of the muffle, a wider range of pigmentary substances is available, as will be seen in the following chapter.

CHAPTER VIII.

MUFFLE COLOURS.

YELLOW PORCELAIN COLOURS.

A LARGE number of substances capable of furnishing yellow porcelain colours are known, with a very wide range of tones; but their selection is by no means a matter of indifference, and it is necessary in all cases, in view of securing a harmonious effect, to use the colour best adapted to furnish an artistic result.

For pure yellow, the following preparations are available:—Pure antimony oxide, potassium antimoniate, lead antimoniate (*i.e.* the artist's colour known as "Naples yellow"), silver oxide, uranium oxide, and to some extent ferric oxide as well. The latter is generally used merely in small quantities as an adjunct to the other colours, since the colour imparted by ferric oxide to the glass fluxes is not yellow, but rather a mixture between yellow, red, and brown, as can be clearly seen in the case of ordinary wine bottles.

ANTIMONY OXIDE.

The preparation of antimony oxide can be carried on in various ways, the object in all cases, however, being to obtain a perfectly pure oxide, free from all extraneous substances, since the presence of even small traces of the latter is sufficient to modify the colour considerably.

The most effectual way is to reduce commercial antimony

trisulphide to a very fine powder and boil this with crude hydrochloric acid so long as any sulphuretted hydrogen is given off. The liquid is then left to stand until quite clear, and the solution carefully decanted from the sediment. The resulting solution of antimony trichloride when poured into a large quantity of water is decomposed with formation of basic antimony chloride, which settles down as a dense, pure white powder.

This white precipitate is transferred to a large porcelain dish and suffused with a solution of 1 part of soda crystals in 3 parts of water, the whole being boiled until it imparts a permanent blue coloration to red litmus paper. The sodium carbonate displaces the chlorine in the basic antimony chloride, and converts the latter into pure antimony oxide, which is washed with boiling water on a filter until all the soluble matter is removed, and is finally dried.

Antimony oxide can also be prepared direct from metallic antimony, by fusing the latter in an open vessel, and continuing to heat it so strongly that the whole of the metal is finally burned to oxide. This operation is generally performed in a slanting crucible, the bottom of which is filled with a certain quantity of metallic antimony. When heated, the metal burns with a peculiar livid blue flame, and the resulting antimony oxide is deposited on the colder portions of the crucible, in the form of small acicular, highly lustrous crystals.

Working in this way, however, a considerable portion of the antimony oxide is lost, to avoid which the operation has been modified by heating the metal in a porcelain basin, over which is mounted a similar basin, inverted, with an interval of a few millimetres between the two. The middle of the inverted basin is pierced by an opening about 2 inches wide, on which is placed a tube of glass or porcelain, terminating above in a large wooden box. The antimony in the lower basin burns, and the vapours ascend through the tube into the box and are deposited

there. When the operation has been continued for some time with a large amount of antimony, the interior of the box will be found coated entirely with the lustrous crystals.

This direct combustion method furnishes a mass that is far from being pure antimony oxide, but rather consists of a mixture of antimony oxide, antimonic acid, and antimony antimoniate.

The best way to prepare pure antimony oxide by the dry method is by detonating a mixture of metallic antimony, potassium nitrate, and potassium bisulphate, the most favourable proportions being—

Metallic antimony	: . . .	37 parts.
Potassium nitrate	20 „
Potassium bisulphate	15 „

The ingredients, in a very finely divided state and perfectly dry, are intimately mixed, and then placed by degrees in a large crucible already raised to a strong red heat, each portion being allowed to detonate and subside before adding the next. When all is in, the crucible is heated as strongly as possible, and the fluid contents are then poured out on to a smooth stone, the solidified mass being afterwards broken into fragments and lixiviated with boiling water in a porcelain basin. After boiling has been continued for some time, the contents of the basin are allowed to settle, and a pure white powder of antimony oxide will be found to have been deposited under the clear liquid. This powder is washed and dried in the usual way.

The foregoing method is used when the preparation is to be employed in the manufacture of very fine colours, but for inferior grades the following process is simpler.

Antimony is powdered and placed in a large glass vessel standing in a large porcelain basin containing a little water, the metal being suffused with very small quantities of nitric acid, preferably with four parts of acid of sp. gr. 1.2 to each 1 part of metal, the acid being diluted with 8 parts of water. The

acid must be added in very small quantities at a time, owing to the violence of the reaction and the danger of the mass overflowing when a larger amount of acid is used.

It is also necessary to perform the operation out of doors, owing to the liberation of poisonous, dense brown fumes. When all the acid has been consumed, the basin containing the glass vessel is carefully heated till the contents of the vessel boil and the final traces of the metallic antimony are oxidised, the powder in the glass vessel being then washed with hot water and dried. It should be mentioned that the product is not pure antimony oxide, but contains small quantities of unaltered metallic antimony and basic antimony nitrate. This circumstance, however, does not affect the colour, provided the preparation is made by exactly the same recipe every time.

POTASSIUM ANTIMONIATE.

A very handsome yellow, which, however, is more suitable for cheap ware, can be prepared in a very simple manner as follows:—

Ordinary grey antimony ore is finely powdered and mixed with half its weight of potassium nitrate, small quantities of the mixture being thrown in succession into a suitably large crucible previously raised to strong red heat, each portion detonating as it is thrown in. When the reaction is finished, the crucible contains a white mass consisting of a mixture of potassium antimoniate and potassium sulphate, together with some undecomposed antimony ore.

The powdered mass is stored in tightly closed vessels, and is more suitable for cheap ware than for porcelain, the colour being inferior to that of the other antimony preparations.

NAPLES YELLOW.

This colour, which is the handsomest and most powerful of all the antimony preparations, consists of lead antimoniate. It

can be prepared in various ways, both the following methods yielding an equally good product.

According to the one method, 1 part of tartar emetic (potassium antimony tartrate) is mixed with 2 of lead nitrate and 4 parts of common salt, as intimately as possible, the mixture being carefully heated to melting-point in a crucible, taking care not to exceed moderate red heat. The molten mass is poured into water, in which the excess of common salt dissolves, leaving the lead antimoniate as a handsome yellow powder in the bottom of the vessel.

In the second method, which some consider to yield a better product, 2 parts of tartar emetic are fused with 4 parts of lead nitrate and 8 of common salt, the molten mass being treated with very dilute hydrochloric acid in order to dissolve out the excess of lead oxide.

In either case the operation has to be performed at a certain temperature, which must not be exceeded. It is for this reason that the common salt is introduced in the mixture, though it takes no part in the reaction, its functions being confined to keeping the temperature of the molten mass within certain limits. This it does by volatilising at moderate red heat, and so long as any salt remains in the mass the temperature will not rise above the volatilising point of the salt.

When the heat applied has been just sufficient to melt the mixture, the product will be orange red in colour, but higher temperatures give a progressively paler colour, ranging through lemon to sulphur yellow.

SILVER YELLOW.

This is a very handsome yellow for porcelain, but entails great care in preparation. It can be obtained either from pure silver oxide or silver chloride. In the former case, the method is as follows:—

A solution of chemically pure silver nitrate, diluted with dis-

tilled water, is placed in a large glass vessel and treated with caustic potash, with constant stirring, so long as a precipitate continues to form. The silver oxide is collected on a filter, washed repeatedly with boiling water, and dried. When the colour prepared from this oxide is fired on the ware, a silvered surface is obtained, the oxide having been reduced to metallic silver on the surface, whilst underneath a deep yellow colour is formed. The thin superficial film of silver can be removed by mechanical means, but preferably by brushing it over with very dilute nitric acid, the dissolved silver being then swilled off thoroughly with water.

Silver yellow can also be produced from silver chloride, prepared by treating silver nitrate solution with dilute hydrochloric acid in a dimly lighted room, so long as a curdy white precipitate continues to form. This precipitate, which is silver chloride, is washed, dried, and stored in a black or red glass vessel, since, when exposed to ordinary daylight, it would quickly turn violet and then black, the chloride being decomposed by sunlight. The mixture of silver chloride and powdered flux must also be prepared by artificial light and kept in the dark.

URANIUM YELLOW.

Uranium oxide imparts a very handsome wine yellow colour to glass fluxes, the glass stained by this oxide exhibiting a very fine canary-green fluorescence when viewed by reflected light. Since uranium oxide is used in porcelain painting as a yellow pigment exclusively, mention must be made of the fact that its tinctorial power is so great that 1 part by weight is sufficient to colour 200 parts of flux a deep yellow, so that great care is necessary in compounding colours with this pigment.

RED PORCELAIN COLOURS.

A fairly large number of colours are available for producing the different kinds of red used in porcelain painting, all those

already mentioned for earthenware underglaze red being applicable. In addition to these come a few that can only be used as muffle colours, *e.g.*, coral red, gold purple, and ruby glass.

Special attention is merited by the iron reds, which, in addition to being cheap, furnish a wider range of tones than is known in the case of any other oxides used as porcelain colours, the shades varying from a pale yellowish red, through blood red, to deep violet.

These tones can be obtained from pure ferric oxide by varying the time of exposure to strong red heat. This modification of treatment is easy in porcelain works, inasmuch as the crucibles charged with pure ferric oxide can be fired one or more times in succession in the glost kiln.

The colour scale of the ferric oxide colours can be considerably amplified by the addition of aluminium oxide in varying proportions. The method of preparation is the same as that already described in the case of earthenware colours.

In order to obtain a definite colour scale, which can be imitated whenever required, it is advisable to proceed in the following manner:—

An aqueous solution of ferric chloride is prepared by dissolving an accurately weighed quantity of crystallised ferric chloride in a measured volume of water; and, on the other hand, a solution of aluminium acetate of known density is got ready.

These two solutions are then mixed, in the proportion of 10 parts of the former to 1 of the latter, and the mixture is precipitated with sodium carbonate solution, the precipitate being thoroughly washed with boiling water, dried, and calcined at a fairly constant temperature; for the purpose of muffle colours a strong red heat is sufficient.

In a second trial, 10 parts of the ferric chloride solution

are mixed with 2 parts of the aluminium acetate solution ; in a third, 3 parts of the latter are used, and so on. The precipitates, when washed, dried, and calcined as above, give tones varying with the relative proportions of ferric oxide and alumina, the shades ranging from red to pale red on the one hand, and to brown violet on the other.

By substituting a solution of magnesium sulphate for the aluminium acetate in the mixture with ferric chloride, another class of colours is obtained ; and another modification is obtained by using both the sulphate and acetate in question along with ferric chloride, the precipitate being in all cases washed, dried, and calcined as described.

In this way a whole series of red, brown, and violet colours can be prepared with very little trouble and expense. All these colours are well adapted for use on porcelain, and enable the painter to quickly select the shade he desires, from the specimen tiles, all that is then necessary being to obtain from stock the corresponding number ready for use.

CORAL RED.

This porcelain colour consists of basic lead chromate, and is prepared by treating a solution of lead acetate with one of potassium bichromate so long as a precipitate continues to form. This precipitate is a fine yellow, and forms the pigment known as chrome yellow. When boiled with a not too concentrated solution of caustic soda, chrome yellow parts with a portion of its chromic acid, the colour of the compound passing over, through orange red, to a very fiery coral red.

After the mass has been boiled with water, washed and dried, it forms a dense powder, which, when mixed with a corresponding amount of readily fusible lead glaze and applied to porcelain, is distinguished by unusual brightness of colour.

GOLD PURPLE.

This preparation—also known as purple of Cassius—is of great value in porcelain painting, since it enables a whole series of reds to be obtained that cannot be produced by any other means.

The composition of gold purple is apparently variable, depending on the method of preparation, so that, in order to obtain a uniform colour, it is necessary to work always in the same way. A number of these methods are detailed below, and the intending user of gold purple is recommended to try them in succession until he meets with the one he prefers.

It is, however, necessary to mention beforehand that purple of Cassius must always be made from a solution of gold trichloride, which must be as nearly as possible neutral and entirely free from nitric acid, since the presence of even the slightest trace of this latter would spoil the character of the product. As the preparation of gold trichloride will have to be described in detail when dealing with the decoration of porcelain by the aid of metals, all that need be mentioned at present is that the gold purple will, as a rule, be finer in colour in proportion to the degree of dilution of the solutions employed in its preparation.

GOLD PURPLE, ACCORDING TO FUCHS.

A clear solution of stannous chloride in water is poured into a solution of ferric chloride, until the yellow-brown colour of the latter has turned green. On the other hand, a solution of gold trichloride is diluted with 300-400 parts of water, and into this solution the green liquid is poured with constant stirring. The liquid turns brown, and on being left to stand for a day, deposits a brown precipitate, which is filtered off, washed several times in clean water, and dried.

This method will only give good results when the gold

solution is sufficiently dilute, a condition revealed by the following test. Before commencing to pour the tin solution into the gold solution, a glass rod is dipped into the former, and then into the gold solution, whereupon a brown precipitate should form about the rod, but immediately redissolve and impart a wine-red coloration to the surrounding liquid. The refusal of the precipitate to dissolve indicates that the gold solution contains too little water and must be further diluted.

BOLLEY'S GOLD PURPLE.

A solution of stannic ammonium chloride is left in contact with granulated tin for several days and then treated with very dilute gold chloride solution, whereupon the purple will separate out in a short time.

FIGUIER'S GOLD PURPLE.

According to this recipe, gold purple is prepared in the dry way by fusing a small quantity of anhydrous borax in a crucible, heating it to redness, and then introducing 150 parts of chemically pure silver, 20 parts of gold, and 35.1 parts of tin, the temperature being afterwards raised so that the metals combine to form a homogeneous alloy. When the crucible is cold, the contents are boiled with hot water, to dissolve out the borax, and the fragments of metal are immersed in dilute nitric acid, which dissolves out the silver, whilst the gold and tin combine, with absorption of oxygen, to form gold purple.

SCHNITZLER'S GOLD PURPLE.

One part of crystallised stannous chloride and 2 of crystallised stannic chloride are dissolved separately, and the mixed solutions are poured into a very dilute solution of 1 part of gold chloride. A purple precipitate is formed, which gradually subsides, the deposition being accelerated by adding alcohol.

WAECHTER'S GOLD PURPLE.

We are indebted to this chemist for a number of recipes for the preparation of gold purple, all of considerable importance for our purpose, since, by following his instructions, various shades of purple can be obtained.

DARK GOLD PURPLE.

Half a gramme of gold is converted into gold trichloride, and the solution, diluted with 10 litres of water, is treated with a solution of 7.5 grms. of stannous chloride. After adding a few drops of sulphuric acid, the precipitate is allowed to settle down, and when dry is mixed with 0.5 gm. of silver carbonate and 10 grms. of lead flux.

LIGHT PURPLE.

Five grammes of tin are dissolved in hot nitro-hydrochloric acid (a mixture of 3 parts of hydrochloric acid and 1 of nitric acid), the solution being evaporated on the water bath until solid and all the free acid has been vaporised. The residue is dissolved in distilled water, mixed with a solution of 2 grms. of stannous chloride (sp. gr. 1.7), diluted with 10 litres of water, and treated with a solution of 0.5 gm. of gold and 50 grms. of ammonia. The liquid turns deep red and soon deposits a precipitate, which is washed, and while still moist, mixed with 20 grms. of lead flux of the composition given below, the dried powder being treated with 3 grms. of silver carbonate.

The lead flux is prepared by fusing together 1 part of quartz sand, 1 part of calcined borax, and 2 parts of red lead. The resulting purple is of a pale colour: and an amethyst shade can be obtained by omitting the silver carbonate.

ROSE PURPLE.

A solution of 1 gm. of gold, in the form of gold trichloride, is mixed with a solution of 50 grms. of alum, and treated with

1.5 gm. of stannous chloride solution (sp. gr. 1.7), ammonia being then poured in as long as a precipitate continues to form. This precipitate is washed, dried, and mixed with 70 grms. of the above lead flux and 2.5 grms. of silver carbonate.

In addition to the purple of Cassius, consisting of gold oxide and tin oxide, gold purples can be prepared by means of magnesium or aluminium oxides.

MAGNESIA PURPLE.

Magnesia is levigated in water to form a thin milk, and is heated to near boiling with a solution of gold trichloride, the washed precipitate being afterwards dried and heated to redness.

ALUMINA PURPLE.

An aqueous solution of potassium alum is mixed with one of gold trichloride and precipitated with ammonia, the precipitate being washed, dried, and calcined.

RUBY GLASS.

This is the name applied to a perfectly transparent glass, of exactly the same tint as the ruby. This glass possesses special importance for the porcelain painter, since it enables a wide range of colours to be obtained, from the palest pink to the deepest ruby red.

According to the method of preparation adopted, two kinds of ruby glass are known: gold ruby glass and copper ruby glass, the former containing metallic gold in a special form of solution in the glass; the other being coloured by metallic copper. For porcelain painting it is immaterial which of these glasses is used, both furnishing exactly the same colour in use.

At one time gold ruby glass was very high in price, on the pretext of its content of the expensive metal, gold. This, however, is unjustifiable, 1 part of gold being sufficient to

transform 50,000 parts of glass into deep ruby glass. The tinctorial power of gold toward glass is so powerful that even 1 part in 100,000 will give a light red glass.

Moreover, the solvent capacity of glass for gold is very small, and if an excess of gold be taken designedly, the glass will only dissolve sufficient to give a deep ruby glass, the surplus gold being left behind as a fused button in the bottom of the crucible.

GOLD RUBY GLASS.

A number of recipes for making handsome gold ruby glass are known, but it will be sufficient for our purpose to give only a few of the easiest. The gold must always be in the form of trichloride (obtained by dissolving gold in nitro-hydrochloric acid), and used as a very dilute solution. This solution is sprinkled over the quartz sand used in the charge of glass metal, the sand being well stirred to ensure that all the particles are wetted with the solution: and it is only when this has been accomplished that the rest of the glass ingredients are added. The glass metal is compounded according to Cohn's formula, namely:—

Quartz sand	300 parts.
Red lead	375 „
Potash	75 „
Potassium nitrate	50 „

Minted gold may be used for preparing the solution, the small amount of copper present having no injurious influence on the colour.

The finished molten glass must be heated as high as possible, to convert the gold into the modification which stains the glass red; otherwise only a leather-brown glass will be obtained.

Finished ruby glass is colourless when cold, and it is only on being reheated that the red coloration appears.

According to another recipe by Fuchs, gold ruby glass may be prepared by melting a charge of glass metal composed of—

Quartz	5 parts,
Red lead	8 „
Potassium nitrate	1 part,
Potassium carbonate	1 „

the molten glass being run out of the furnace into cold water. The powdered melt is mixed with the following ingredients:—

Melt	4000 parts,
Crystallised borax	750 „
Tin oxide	25 „
Antimony oxide	25 „

and sprinkled with gold solution.

The charge is fused in a crucible for twelve hours, and then allowed to cool in an annealing oven. The mass broken out of the crucible is topaz yellow in colour, but soon turns deep red when reheated.

COPPER RUBY GLASS.

Like gold, metallic copper has the property of dissolving to a ruby red colour in glass, in certain circumstances. In preparing this glass it is important to give the glass metal such a composition that the copper is obliged to remain in the metallic state, since, if it were converted into oxide, the colour would be blue or green, and not ruby.

Ferric oxide is generally selected as the reducing agent to prevent the copper being oxidised. For ruby glass the proportion of copper in the metal should not exceed 2 per cent., a larger quantity producing a blood red colour (“hæmatinone”).

According to Stein, the following charge of glass metal is suitable for ruby glass:—

Quartz sand	100 parts.
Red lead	166 „

Ferric oxide	10 parts.
Copper ash	7 „

The ferric oxide may also be replaced by 7 parts of tin ash.

Another glass metal, which also furnishes good results, is compounded of—

Quartz sand	100 parts.
Red lead	200 „
Copper ash	6 „
Tin ash	6 „

The charge is fused for twelve hours, and repeatedly stirred with a stick in order that the reducing vapours liberated by the wood may prevent the oxidation of the copper, whilst at the same time the ingredients are intimately mixed. The finished glass is granulated in water and remelted, the colour developing in this operation just as in the case of gold ruby glass.

GREEN PORCELAIN COLOURS.

Several substances capable of imparting a green coloration to glass are known, namely, uranium oxide (already mentioned in connection with yellows), ferrous oxide, copper oxide, and chromic oxide.

The use of ferrous oxide for porcelain painting is, however, precluded on account of its powerful reducing action, so that when applied to porcelain with a lead flux and fired, it would undergo conversion into ferric oxide and produce a bottle-brown colour.

Copper oxide stains glass fluxes a peculiar bluish green, but is rarely used, owing to its liability to go wrong in the firing process.

Chromic oxide is the colour most generally employed for green on porcelain, since it furnishes a perfectly pure green, entirely free from traces of any other tone, and can be employed as the standard pure green in the colour scale. Since the

chrome greens can be shaded to any desired extent by the addition of yellow on the one hand, and blue on the other, they are sufficient for all the purposes now in question.

Mention should be made of the special peculiarity of chromic oxide, of dissolving in considerable quantities in molten glass, and of undergoing partial deposition when the temperature of the glass metal sinks below a certain point. It separates in the form of microscopic crystals, and imparts to the glass the appearance of the so-called chrome aventurin glasses, the matrix of green glass containing minute crystals of chromic oxide, which cannot be seen by the unaided eye, and reflect the light in a curious manner, imparting a peculiar appearance to the glass. This effect being undesirable in porcelain painting, care must be taken in preparing the chrome-green colours to avoid using more than a certain amount of chromic oxide.

BLUE PORCELAIN COLOURS.

All blue colours for porcelain are prepared from cobalt compounds, and consist chiefly of a substance coloured blue by cobalt oxide, which substance must be regarded as a glass. The simplest way to prepare it is by fusing either pure cobalt oxide or cobaltic carbonate with pure quartz sand, zinc oxide, and sodium carbonate. The blue colour of the resulting glass depends on the amount of cobalt oxide and zinc oxide present in the mixture.

The higher the relative proportion of the cobalt compounds, the darker the colour of the glass, the completely fused mass having the appearance of a black substance, which only transmits a dark blue light through the sharp-edged surfaces of fracture.

The colour pastes made in glass works consist of fusible glass, preferably a fusible lead glass deeply stained by means

of large quantities of pigmentary oxides. Similar colour pastes are also suitable for painting on porcelain, a readily fusible lead glass being melted with a weighed quantity of cobalt oxide in a porcelain crucible. The fused mass is poured into cold water, in which it quickly solidifies and becomes so brittle as to be easily reduced to fine powder. After the mass has been pulverised as finely as possible in the dry state, it is levigated until an impalpable powder is obtained.

This powder, which gives the darkest shade of blue that is possible to obtain, is next mixed with varying proportions of flux and fired on test plates of porcelain, thus enabling the colour furnished by a given mixture of blue mass and flux to be determined beforehand.

Since, as already mentioned, the blue mass is itself a glass, it melts to a uniform mass when fired along with the flux; and even large surfaces can be painted with these colours without showing the slightest inequality in shade.

The pure blue obtainable from cobalt oxide exclusively, can be easily modified in various ways. As a rule, these shaded colours are prepared only at the time of use, by mixing, for instance, a yellow with a blue, and thus imparting a greenish tinge to the pure blue. The addition of a certain quantity of red will give a purple tint, which may be further modified to violet.

Fairly large quantities of alumina are also frequently used in the preparation of cobalt blues, their addition giving the colour a greenish cast. The usual reason for these additions, however, is not to modify the shade, but to enable the colour to stand greater heat and fit it for use as an underglaze colour.

The fluxes employed for the blue cobalt colours must always be free from alkali, the presence of the latter invariably exerting an unfavourable influence on the beauty of the colour. Preference is given to the pure lead fluxes, or such as contain

a certain quantity of boric acid. In order to prevent the said injurious influence on the colour, the amount of soda used in preparing the aforesaid glass pastes must be reduced to a minimum, so that the resulting glass mainly consists of lead silicate. To increase the fusibility, a certain amount of boric acid is added to the glass metal in the making, in place of an equivalent quantity of silica.

GLOST FIRE BLUE.

Though all the blue ceramic colours contain cobalt oxide, they often differ considerably in tone—even when prepared from pure oxide—under different firing temperatures, though one and the same preparation has been used. The reason for this peculiar phenomenon is that certain cobalt colours are very susceptible to the reducing action of the fire gases that cannot always be excluded, despite all the care taken, so that some of the oxides are reduced to a lower stage of oxidation and the colour comes out different from the shade desired.

The surest way to rectify this defect is by using a colour composed of cobalt oxide and magnesia, or preferably alumina. Some potters think that the better results are obtained by replacing those oxides by ground porcelain or pure kaolin, but this is not in accordance with fact.

A compound of cobalt oxide and alumina can be prepared in which these two oxides are so firmly combined that even a prolonged exposure to the action of reducing gases cannot alter the tone of the colour.

We will now give a few recipes that are employed in many works for producing a resistant blue colour, and will then describe the methods that seem preferable to the author.

One part of cobalt oxide is mixed with 1-3 parts of pure precipitated alumina, or with 1 part of calcined magnesia, or 1 part of pure kaolin. The very finely powdered oxides must be mixed with great care, and the mixture then exposed to as

high a temperature as possible, the resulting mass being afterwards ground along with one-third its own weight of ground glaze mass. Some makers add a certain amount of potassium nitrate to the mixture, to prevent the reducing action of the fire gases in the kiln by disengaging oxygen; and in some works the finished colour is boiled with a 5 per cent. solution of potassium nitrate, and finally evaporated to dryness. By working in this way the potassium nitrate is not decomposed until the colour is fired on the ware (these colours are generally used under glaze), the residual potash passing into the glaze.

COBALT BLUE BY THE WET METHOD.

The handsomest and most uniform cobalt blues are obtained from the combination of cobalt oxide and alumina, prepared by the wet method, the colour being the Thénard's blue, so long esteemed by artists as the finest and most durable colour of its kind. The method of preparation is as follows, the product being always of uniform character:—

Twenty-three parts of anhydrous cobaltous sulphate are dissolved in water, and mixed, by stirring with a glass rod, with another aqueous solution of 166 parts of aluminium sulphate, the mixture being treated with a solution of sodium carbonate (free from iron) so long as a precipitate continues to form. The precipitate is collected on a filter, well washed with hot water, and dried at a temperature which can be raised to incipient red heat, after which it is stamped solid in an unglazed porcelain crucible. The latter is then covered with a projecting lid and placed in a Hessian crucible, in which it is brasqued with powdered manganese dioxide, and the whole is exposed to the highest temperature of the glost kiln.

When cold, the contents form a deep blue mass consisting of a stable chemical compound of the formula: $5\text{Al}_2\text{O}_3 + 3\text{CoO}$,

and the combination will be the more intimate the higher the temperature during the heating process. The object of brasquing the crucible with manganese dioxide is to prevent any reducing action by the furnace gases, the dioxide liberating oxygen when heated.

By mixing certain proportions of this blue mass with a glaze of constant composition, any desired shade of blue can always be obtained; and it is advisable to use this colour invariably for producing the so-called onion pattern on porcelain, since by this means failure is precluded.

COBALTOUS ZINC PHOSPHATE.

This preparation, which is distinguished by its very handsome, peculiar blue tone, can be easily made by treating a solution of ordinary sodium phosphate with a solution of zinc sulphate so long as a white precipitate continues to form. The liquid is then stirred up well with a solution of cobaltous sulphate, added progressively until the colour of the precipitate has changed to a deep blue.

Used alone with flux, cobaltous phosphate yields a very fine blue of peculiar tone, which can be shaded as desired by additions of pure cobaltous oxide or some other blue cobalt colour.

COBALTOUS SILICATE.

This very handsome and stable colour can be easily prepared by treating a solution of cobaltous sulphate with very dilute sodium silicate so long as a precipitate forms. This precipitate must be repeatedly washed with boiling water to remove any excess of sodium silicate. When dry, the precipitate is fused and poured into cold water to make it easy to pulverise. The preparation yields very handsome, pure blues, the depth of which depends on the amount of flux added.

VIOLET PORCELAIN COLOURS.

The only pure violet colours obtainable for porcelain painting are those from manganese compounds. It is frequently stated in works on the subject that a very fine violet can be prepared from selected lumps of manganese dioxide (the mineral pyrolusite), reduced to a fine powder and mixed in suitable proportions with flux. The author, however, wishes it to be distinctly understood that he has never succeeded in obtaining a perfectly violet in this way, even from the finest specimens of the mineral. The colour is never pure, especially in the lighter shades, but always contains some extraneous admixtures. This is easy to understand when it is remembered that the presence of minute traces of foreign oxides greatly influences the colour, and that ferric oxide is never absent from even the finest lumps of the mineral.

To obviate this defect the author recommends the use of perfectly pure manganese preparations, such as are obtained by the method described below, the more so because, in view of the powerful tinctorial properties of manganese, the amount of the pure manganese preparation required for a large quantity of porcelain colour is very small.

A fine specimen of manganese mineral is taken, reduced to fine powder and boiled with hydrochloric acid in a porcelain dish until the liberation of chlorine gas ceases, the operation being conducted under a chimney with a good draught on account of the injurious action of the gas on the respiratory organs. The result is a brown solution of manganous chloride, which must be filtered for further treatment. It should be stated that this crude manganous chloride solution can be purchased from works in which chlorine is manufactured from manganese dioxide and hydrochloric acid, the chloride being left as a by-product.

A solution of potassium hypochlorite is prepared by suffusing

bleaching powder with water, stirring up the mixture, and, after leaving it for half an hour, filtering the solution into that of the crude manganous chloride.

The contact of the two liquids results in the immediate formation of a deep brown precipitate, which continually increases in quantity, whilst at the same time the previously dark brown liquid becomes paler and paler, until at length it is merely stained pale yellow from the dissolved ferric oxide. The precipitate, which quickly settles down, consists of hydrated manganese peroxide and is of a deep brown colour. It is collected on a filter, washed out well with hot water, dried, and carefully heated to about 150–160° C., whereby the water of hydration is expelled and manganese peroxide is left.

Since the presence of even a very small quantity of organic matter is sufficient to considerably affect the colour developed by manganese, the finished oxide must be immediately placed in tightly closed vessels, the least trace of atmospheric dust being very injurious.

Great care is also necessary in firing manganese violet on the ware, and the operation must be always conducted in muffles effectually protected against the influx of reducing gases, the latter either spoiling the violet entirely, or else making it much weaker than it should be.

Finally, it must be remarked that the tinctorial power of manganese is so strong that the oxide can even be employed for producing a fairly pure black. All that is necessary for this purpose is to use a very large quantity of manganese peroxide in proportion to the flux, and a perfectly black looking mass will be obtained. As a matter of fact, this mass is violet in colour, as can readily be ascertained by examining a very thin splinter by transmitted light; but the violet is so deep that it appears black to the eye.

Consequently, as will be mentioned later in dealing with

the black porcelain colours, a certain amount of manganese peroxide is used in their preparation along with other oxides.

A very handsome violet can also be obtained with purple of Cassius, by adding a suitable quantity of cobalt oxide.

BROWN PORCELAIN COLOURS.

No single pigment capable of producing brown colours on porcelain is known, a mixture of various oxides being necessary in all cases. Hence, in order to be able to obtain any definite shade of brown, it is essential to employ known quantities of pigmentary oxides in the mixture. The number of shades of brown, however, is so large that it is impossible to give recipes for them all, and the correct proportions to use for any desired shade must be ascertained by experiment.

Light brown colours are usually prepared by mixing iron-red colours with varying proportions of zinc oxide, and occasionally with a little nickelous oxide as well.

For darker shades of brown the iron reds are mixed with manganese oxide or ochre, toning the mixture if necessary with nickel oxide.

The addition of a certain quantity of cobalt oxide to these mixtures will give a brown so deep in colour as to appear nearly black; and a pure deep black is obtained by the further addition of pure chromic oxide or ferric chromate. It should, however, be noted that great care is necessary in adding these auxiliary pigments, cobalt oxide, chromic oxide, and ferric chromate, when a brown colour is desired, their tinctorial power being so great that they mask the fundamental colour if used in excess.

BLACK AND GREY PORCELAIN COLOURS.

The black porcelain colours consist of the mixtures just mentioned, though iridium oxide is also suitable, furnishing a

very handsome but expensive black. For this reason it is rarely employed.

The easiest way to prepare grey is by mixing one of the above blacks with a corresponding amount of zinc oxide; the larger the proportion of the latter the paler the grey.

Instead of zinc oxide, some porcelain painters use flux direct, to turn the black into grey.

The finest grey, and one that will mix well with other colours, is obtained from finely divided metallic platinum; but of course this very expensive colour can only be used for the finest work.

ENAMEL COLOURS.

The colours just described are those generally employed for decorations that are to be fired in a muffle. In addition, for the production of certain effects, the porcelain painter employs other colours differing from the foregoing in that they do not allow the white substance of the ware to show through, but are opaque.

The colours used for this purpose are known as enamel colours, and they differ in composition from the previously described porcelain colours in containing such a large proportion of tin oxide that they form an opaque mass when fired. This gives the colours an entirely different appearance, the change being on a par with that already mentioned in connection with cobalt blue, which when mixed with a sufficient amount of flux gives a more or less deep sky blue, but is modified into turquoise or forget-me-not blue by an addition of tin oxide.

A point to be borne in mind in the preparation of the muffle colours is the relative fusibility of the various colours themselves. It is desirable that all the colours employed in producing a decoration should have about the same fusing point, a condition that is not easy of fulfilment, owing to the necessity

of using different fluxes, with varying fusing points, for different colours.

The temperature necessary in any given case may be ascertained by a trial, taking care to avoid excessive heat, as this tends to alter the shade of certain colours.

In order to test the colours in this way, a smooth porcelain tile is painted over with the colours to be used, and is then fired in a small muffle covered with a lid provided with a peep-hole. The point at which any of the colours are sufficiently fired is indicated by their sudden glossing, due to the melting of the flux; and so long as any of the colours remain matt on the tile, they are not done, the glaze not having fused.

To obviate the injurious effect of a too protracted high temperature on the delicate colours, it is usual, in the firing process, to warm the ware strongly at first, without, however, raising the temperature to the melting point of even the most fusible flux, and only then increasing the heat for a short time to a point at which the most refractory of the fluxes is melted. This precaution is adopted for the sole purpose of preventing the cracking of the ware, the risk of which is considerable when high temperatures are employed from the start.

PREPARATION OF THE MUFFLE COLOURS.

The operations in this process comprise: powdering the colours, mixing them with the necessary amount of flux, and incorporating them with the liquid medium enabling them to be applied to the ware.

The reduction of the colours to powder must be effected with great care, the production of an impalpable powder being essential, so that no coarse granules can be detected when the powder is examined with a magnifier. Should any such granules be present, the inevitable result would be the formation of dark specks on the ware.

Colours that are unaffected by contact with large quantities

of water may be ground in a wet mill, this method being also adopted for the fluxes. The powdered colours and fluxes are incorporated by protracted trituration, so as to form a perfectly homogeneous mixture.

The medium generally used for bringing the mixed colour and flux into a workable consistency is oil of turpentine, the powder being spread on a sheet of glass, the requisite quantity of turps poured on to it, and the whole mixed to a uniform wash by means of a glass muller.

This troublesome task, however, is now generally superseded by the use of colour mills, the mixing being performed between two closely set plates or a pair of cones one of which fits accurately inside the other. The contact surfaces of these mills must in all cases consist of porcelain, since even the smallest particle of metal from the plates or cones would spoil the colour. If roller mills are used, the rollers must be made of porcelain.

The finest rectified oil of turpentine is a liquid which, when exposed to the air in thin layers, quickly evaporates without the slightest trace of residue. If such oil of turpentine were used alone for mixing the colours, the latter would adhere very imperfectly to the smooth surface of the glaze, and easily drop off as soon as the medium evaporated. For this reason it is customary to add to the oil of turpentine a small percentage of thickened oil, prepared as described below, in order to impart viscosity to the wash and enable the dried colour to adhere sufficiently to the ware.

About two quarts of rectified oil of turpentine are placed in a clear glass bottle, holding about $2\frac{1}{2}$ gallons, the bottle being tightly corked and set in a very sunny place. In the course of a few days, the turpentine will be observed to have turned yellow and become appreciably thicker. The thickening process can be greatly accelerated by blowing fresh air into the bottle about once a week; and in a few months' time the oil will have become converted into a semi-solid mass.

In presence of atmospheric oxygen and direct sunlight, the oil of turpentine takes up oxygen (the latter having first been converted into ozone) and begins to resinify; in fact, if left long enough, it would be completely changed into resin. From time to time a certain amount of this thickened oil may be removed from the bottle and mixed with pure oil of turpentine, to form a kind of varnish which will make the colours sufficiently adhesive when applied to the ware. A small percentage of the thickened oil is sufficient for this purpose.

The painted ware must be carefully protected from dust until it can be transferred to the muffle for firing, since otherwise the organic matter in the dust would be carbonised and exert a reducing effect on some of the colours, thus entirely spoiling their appearance.

CHAPTER IX.

DECORATING PORCELAIN WITH METALS.

IN addition to colours and lustres, porcelain can be decorated with the aid of certain metals, thus imparting a greater richness of appearance than is possible by any other means. Since the metals must also be fired on the ware, it naturally follows that only such metals can be used as will stand heating in the air without undergoing oxidation.

This condition is only fulfilled in its entirety by the metals of a single group, the so-called "noble" metals: gold, silver, and platinum. It is true that aluminium also can be heated to a relatively high temperature without oxidising; and numerous attempts have therefore been made, but apparently without success, to apply this handsome bluish-white metal in the decoration of porcelain on the same lines as the noble metals. If this were possible it would mark a distinct advance, the metal being obtainable at a very low price.

The noble metals for use on porcelain must always be in an extremely fine state of division, so fine, indeed, that it can only be obtained by chemical means. They must be employed either in the state of powder or in certain forms of solution.

Both these can be obtained in commerce, but the prices asked are so high that their preparation in the works is advisable when any but the very smallest quantities are used. For this reason we shall devote a section to the methods by which the porcelain painter can make his own preparations for metallic decoration.

There are two ways of decorating porcelain with metal: in the one, the metal after firing remains matt and devoid of lustre until burnished; whilst in the other, in which certain solutions of the metals are used, the lustre appears at once after firing. Since this method obviates the troublesome operation of burnishing, it is gradually replacing the latter except for very expensive ware, in which special effects can be obtained by burnishing part of the metal and leaving other portions matt.

MAKING GOLD PREPARATIONS.

The preparations used for gilding porcelain are gold trichloride, metallic gold, and the so-called gold-sulphur balsam. To obtain these preparations in a suitable condition it is essential that chemically pure gold should be used, since the presence of even minute traces of foreign metals will prevent the formation of the true gold colour, spoiling the tone and causing changes due to oxidation. The only exception to this rule is in the cases of an alloy of gold with another noble metal, *e.g.*, a very small quantity of rhodium.

Commercial fine gold, though classed as chemically pure, is not absolutely so, but contains certain, if very minute, traces of foreign metals. Hence to obtain the perfectly pure article required for our purpose, the porcelain decorator must prepare the fine gold himself.

THE PREPARATION OF CHEMICALLY PURE GOLD TRICHLORIDE AND METALLIC GOLD.

Chemically pure gold can be prepared from any commercial form of the metal, such as old coins, broken jewellery settings, etc., cut up into very small pieces with the shears, in order to present a larger surface to the action of the solvent, and thus accelerate solution.

The solvent used must be a liquid that disengages free chlorine, this being the only way in which gold can be

dissolved. Nitro-hydrochloric acid or aqua regia (so called because it dissolves the king of metals), consisting of 1 volume of nitric acid and 3 of hydrochloric acid, is invariably used. Since this mixture decomposes on standing, it cannot be prepared beforehand, but the gold is placed in a glass beaker along with the hydrochloric acid, and the requisite proportion of nitric acid is poured in. The glass beaker should be placed in a porcelain basin containing a little water, so that, in the event of the beaker breaking, the contents will not be lost.

Solution proceeds at ordinary temperature, but can be greatly accelerated by heat, the porcelain basin being placed on a tripod and the water heated to boiling by means of a spirit or gas flame underneath. When the liberation of vapour from the liquid ceases, a little more nitric acid is added, this being followed by more hydrochloric acid if the disengagement of vapour is not resumed in a short time. The endeavour should be to dissolve the gold with a minimum of acid, since all excess has to be carefully eliminated afterward by a troublesome process of evaporation.

When all the gold is dissolved, a small quantity of fine grey powder may sometimes be observed at the bottom of the glass. This consists of silver chloride, and is a sign that the gold contained silver.

The gold solution has a peculiar yellow colour, a greenish tinge indicating the presence of a considerable amount of copper in the gold. After diluting the solution with a considerable amount of water—to protect the filter paper from corrosion by the acid—the solution is filtered into a porcelain basin, where it is carefully evaporated so that it continually liberates vapour but does not begin to boil. Should boiling occur, a loss of gold will be sustained by the liquid spurting out of the basin. Evaporation is continued until only a very small quantity of brown liquid remains in the basin; and this on cooling will furnish golden brown crystals of gold trichloride. As these

crystals still contain a considerable amount of acid, they must be redissolved in distilled water and carefully reconcentrated to crystallisation point, whereby pure gold trichloride is finally obtained.

To recover finely powdered gold from the trichloride, the latter is dissolved in sufficient water to form a pale wine-yellow solution, and to this is added a filtered solution of ferrous sulphate. The mixture on being stirred turns dark brown, and in a short time a brown powder, consisting of chemically pure gold, is deposited. The solution is tested, to see whether it contains any more gold, by a further addition of ferrous sulphate; and if no precipitate is formed, the whole of the gold has been already removed.

After waiting until the liquid is again quite clear and transparent, the greater portion is decanted, and the gold powder is collected on a filter, on which it is washed with distilled water until the washings run away quite colourless, whereupon the filter is covered with paper and the gold powder left to dry.

The resulting chemically pure gold is an extremely delicate and very dense powder, of a peculiar brown colour, and possessing the property of assuming the lustre of metallic gold when rubbed by means of a hard substance, such as a burnishing iron on a glass plate. Under the microscope the powder is seen to consist of innumerable tiny crystals.

This gold powder is mixed with the proper quantity of a suitable flux, applied to the ware and fired, the resulting matt surface acquiring the ordinary gold lustre when burnished.

BRIGHT GOLD.

A gold preparation which furnishes a bright surface at once when fired on the ware can be obtained in various ways. The old process for this purpose, however, gave such a thin coating that it resembled a lustre with a golden sheen rather than solid

gilding. More recently, a preparation, known as bright gold solution, has been put on the market, and really furnishes good results. It consists of a clear brown liquid, fairly thick in consistency and with an agreeable aromatic odour. The proportion of gold it contains is about 12 per cent., together with about 1 per cent. of rhodium based on the weight of gold present. This latter metal is the cause of the gold becoming bright, without burnishing, when fired. A number of other metals are also present in the solution, especially bismuth, uranium, chromium, and iron, all in the condition of resins. The alloy of gold and rhodium itself is in the form of a compound (auroterpene sulphide), which is readily soluble in ethereal oils.

When gold sulphide is dissolved in balsam of sulphur, and the solution is suitably diluted with a volatile ethereal oil—oil of turpentine or lavender oil—a solution furnishing bright gold is obtained; but this solution is attended with the drawback that, even when stored in the dark, it rapidly decomposes, with deposition of metallic gold, and therefore must be freshly prepared for use every time.

A solution of gold trichloride, treated with a solution of soap made from soda and pine resin, gives a precipitate which may be regarded as gold resinate: and when this compound is dissolved in oil of turpentine or lavender oil, and fired on porcelain with the requisite amount of flux, a bright gold is obtained.

BALSAM OF SULPHUR.

The chief factor in obtaining a quick drying bright gold is the use of a preparation known as balsam of sulphur. This substance may be prepared in various ways, one of them, giving good results, being as follows:—

Sixteen parts of Venice turpentine and 80 of rectified oil of turpentine are placed in a carefully warmed porcelain

dish (a gas flame being preferably used), and heated with care until a homogeneous liquid is obtained. Sixteen parts of finely powdered sulphur are then stirred in, the stirring and warming being maintained until the whole is dissolved. The process is facilitated by the gradual addition of 50 parts of oil of spike lavender.

The gold solution is stirred into this liquid, at a moderately warm temperature, until all the gold has passed into the balsam of sulphur, and the acid liquid, resulting from the decomposition of the gold chloride, has collected on the top. This liquid is poured off, and the mass is repeatedly washed with hot water, after which it is warmed with 100 parts of oil of turpentine and 65 parts of oil of lavender, until a clear liquid is obtained.

According to Butertro, the gold solution for use with this balsam of sulphur is prepared as follows :

Thirty-two parts of gold are dissolved in a mixture of 298 parts of hydrochloric acid and 128 parts of nitric acid, 1·2 parts of tin and 1·2 of antimony trichloride (butter of antimony) being added, and the whole mixed with the balsam of sulphur. The gilding furnished by this preparation leaves nothing to be desired in point of brightness, but the layer of gold is very thin, so that it soon wears off in use.

A fine, durable bright gold can be produced by mixing gold chloride with a liquid containing, in addition to a certain amount of chromium resinate, a little basic bismuth nitrate. The proportions are as follow :

Gold trichloride	100 parts.
Lavender oil	900 „
Basic bismuth nitrate	5 „
Chromium resinate	50 „

The basic bismuth nitrate is obtained by dissolving metallic bismuth in nitric acid, and pouring the solution into 500-600 times its own volume of water. A pure white substance

immediately separates, which, being very dense, subsides quickly, whereupon it is collected on a filter and washed with water until the washings cease to give an acid reaction. This white substance is basic bismuth nitrate.

The balsam of sulphur described above is viscous, and consequently difficult to manipulate; and, according to Schwarz, a better result can be obtained with the following method:—

Oil of turpentine is exposed to the air until it has thickened and partially resinified, whereupon 50 parts of the same are boiled with 10 of sulphur for some time, the cooled mass being mixed with its own weight of lavender oil. A solution of gold chloride is prepared from 1 part of metal, and mixed with 8-9 parts of the balsam of sulphur by kneading continuously in a mortar. A liberation of hydrochloric acid vapours will be observed.

The mixture may be regarded as finished when it has become viscous and resinous, and no longer sticks to the fingers. It is readily soluble in lavender oil. After standing for twenty-four hours the mass is treated with a quantity of basic bismuth nitrate corresponding to 1 part of this salt for each 2 of gold present. To enable the mass to be filtered it is mixed with carbon disulphide, which renders it sufficiently fluid to pass through a paper filter. The filtered liquid can be left by itself, for the carbon disulphide to evaporate, whereupon it is ready for use.

SILVER PREPARATIONS.

The raw material for the silver preparations used in decorating porcelain is invariably commercial silver, which contains variable proportions of copper. Chemically pure silver is prepared, and can then be used for making the various preparations.

SILVER POWDER.

The pure silver is prepared by dissolving the metal in a minimum of nitric acid, which must be perfectly free from

chlorine compounds, a solution stained blue by the presence of copper being obtained. The liquid is strongly diluted with distilled water and filtered, any brown powder remaining on the filter consisting of pure gold and indicating the presence of this metal in the silver—an occurrence by no means infrequent in the case of old silver coins.

A polished strip of copper is dipped in the clear filtered solution, and is moved to and fro, causing the silver to deposit in the form of a very fine grey powder. The absence of any precipitate on the addition of a drop of hydrochloric acid to the filtered liquid shows that all the silver is down.

The silver powder is filtered off, and washed with hot water until the washings no longer exhibit any colour reaction with a little ammonia. A blue coloration under this test indicates that all the copper has not been washed out. The sufficiently washed silver may be either dried, or else converted at once, in the wet state, into silver nitrate.

SILVER NITRATE.

This salt is obtained by dissolving silver powder in nitric acid, filtering the solution if necessary, and carefully evaporating it in a shallow porcelain dish, without boiling, until a dry solid residue is left, this being then heated until it fuses to a clear liquid which crystallises on cooling. The fusing process is necessary to expel the final traces of nitric acid which are tenaciously retained by the salt.

To prepare silver carbonate from the nitrate, the latter is dissolved in distilled water and treated with a solution of pure sodium carbonate so long as a precipitate continues to form, the precipitate being then washed and dried. It should be noted that all silver preparations must be kept in orange-coloured or black bottles, since direct sunlight causes them to decompose with deposition of metallic silver.

PLATINUM PREPARATIONS.

The platinum preparations used in porcelain painting include, besides metallic platinum, platinum chloride and ammonium platinochloride, which are obtained by dissolving the commercial metal in nitro-hydrochloric acid.

On carefully evaporating the brown solution, brown crystals of platinum chloride are obtained, which are soluble in water, alcohol, and ether. The solution is used for preparing the platinochloride and also the finely divided metal. For the former, the solution of platinum chloride is treated with an aqueous solution of ammonium chloride (*sal ammoniac*), and well stirred. After a short time a dense yellow precipitate settles at the bottom of the vessel, and must be filtered off and washed several times with strong alcohol. When dry, the ammonium platinochloride appears as a yellow powder of high specific gravity.

To prepare the finely divided metallic powder, perfectly dry ammonium platinochloride is placed in a porcelain crucible, which is then carefully and gradually raised to a strong red heat, at which temperature the salt is decomposed, leaving finely divided platinum behind. In this condition the metal is in the form of a velvet-black powder, but changes to grey, with a metallic lustre, under the influence of the burnishing iron.

GILDING, SILVERING, AND PLATINISING PORCELAIN.

BURNISHED GOLD.

When porcelain is to be decorated with burnished gold, the gold powder obtained by precipitation is mixed with a flux, generally consisting of basic bismuth nitrate, in the proportion of 5 to 10 per cent. of the weight of the gold, together with about half that proportion of borax to render the flux more fusible, lead borate being used when the ware is to be fired at a very low

temperature. This last-named salt is obtained by treating an aqueous solution of lead acetate with borax solution, and drying the resulting precipitate.

For inferior ware an endeavour is made to economise in the gold by adding to the latter half its own weight of red mercury oxide, which volatilises without any residue in firing. On the other hand, for expensive ware, in which the fired gilding has sometimes to be engraved, the gold is used without any such admixture; and this thick coating of gold is sometimes termed engraving gold. Matt gold, *i.e.* gold that is not burnished after firing, is produced by applying a mixture of gold and silver, without any flux, and firing at a high temperature, or by intimately tritulating finely ground pure gold leaf with oil of turpentine, applying the mixture with a brush and firing at a high temperature.

Burnished gold may be shaded by the addition of other metals. Pure gold has a reddish tone, but on the addition of a small quantity of silver, a pure golden yellow is obtained, whilst on increasing the silver to about 50 per cent. of the gold, the tone is modified to greenish gold. Finally, an addition of platinum furnishes a beautiful golden red.

The gold may also be used along with small quantities of fusible colours, which tone the metallic lustre, a beautiful bronze being obtained, for instance, by adding a little reddish-brown fusible colour.

The fired gold is always dull, with little metallic lustre, but gradually acquires a faint lustre when rubbed with wet smooth sand. A better plan, however, is to burnish the gold with a glass brush, since the sand easily injures the gilding. To impart the maximum lustre, the gilding must be burnished, at first with an agate burnisher, and finally with one of bloodstone. The gilding can be protected from wear by coating it with a fusible glaze and firing this on. Moreover, to prevent the gold wearing off in use, it must be thickly

laid on, and burnished with special care, the heavy pressure applied to the burnishers flattening the particles of gold, and, as it were, uniting them to form a coherent sheet of metal.

To economise gold, and at the same time produce the appearance of heavy gilding, the parts to be coated with gold may be first painted over with yellow colour, which masks the white background.

For articles of value, in which cost is a minor consideration in comparison with a handsome appearance, for instance richly decorated ornamental vases, very thick burnished gilding is generally employed. An advantage is secured in such cases, inasmuch as parts of the gilding may be left matt, whilst others are more or less highly burnished. In this manner highly artistic effects may be obtained by burnished figuring on a matt ground.

Similar effects can be produced with bright gold, but in such event the porcelain requires special preparation. Thus bright gold only attains its maximum lustre when fired on a smooth glaze surface, but if fired on unglazed ware, on pieces the glaze of which has been roughened or removed, the gilding remains matt.

A simple method of roughening glaze on certain parts of the ware consists in mixing finely ground porcelain sherds with a small quantity of flux, and applying the mixture to, and firing it on, the parts in question. Another way is to catch the surface with hydrofluoric acid, the degree of roughness obtained depending on the duration of exposure to the etching agent. The most delicate way of producing the same result is by covering the ware with a stencil, cut out in the required design, and exposing it in the sand-blast machine, the sand quickly roughening the glaze sufficiently to leave the gilding matt when fired, whilst on the untouched parts it develops its full lustre.

In works where much gilding is done and a particularly

handsome appearance is desired, the deposit of gold can be strengthened by electro-gilding. For this purpose the gold is applied in the usual manner, and when fired, the ware is placed direct in the electroplating bath, in which the gilded parts are connected with the one polar wire, and a plate of gold forms the other electrode. The deposition of gold on the gilding begins immediately, and the thickness of the deposit depends on the length of the sojourn in the bath.

SILVERING AND PLATINISING PORCELAIN.

Porcelain can be coated with silver and platinum in exactly the same manner as described for gilding, the only difference being that finely divided (precipitated) silver or platinum (from ammonium platinochloride) is used.

The decoration may be either matt or bright, as in the case of gold. Silver is now rarely used, the more expensive platinum being preferred, since even the best silvering has little durability, and turns grey or even black in a very short time. This is due to the great affinity this metal has toward sulphur, which is always present—as sulphuretted hydrogen and sulphur dioxide—in the atmosphere, to an extent which, though minute, is sufficient to form the black compound, silver sulphide, which causes the silver to first of all lose its lustre, then turn grey, and finally black. Platinum does not exhibit the fine white colour peculiar to silver, being more of a pale steely grey, but retains its metallic lustre intact on exposure to the air.

There is only one way to preserve the metallic lustre of silver on porcelain, namely, by placing the fired ware in a gold plating bath and covering the silver, by electrolytic means, with an extremely thin deposit of gold, which, without masking the colour of the silver, protects it against the injurious action of sulphur compounds. Care is, however, necessary in handling silvered ware treated in this way, since, if wiped

even with the softest of cloths, the gold facing will be soon abraded and the exposed silver will tarnish.

As in the case of gold, metallic silver and platinum are applied in a mixture with a suitable amount of basic bismuth nitrate, and fired. Bright silver and platinum are also produced by preparing the mass with balsam of sulphur, as already described for gold.

CHAPTER X.

DECORATING PORCELAIN BY ELECTROPLATING.

SINCE the introduction of the sand blast into ceramics, fine faience ware, and more especially porcelain, can be decorated by electroplating. The author was the first to apply this method of decoration, which yields very handsome effects, the *modus operandi* being as follows :

The completely finished porcelain or faience ware is covered with stencils of thick, soft paper in such a manner as to leave exposed only the parts to be decorated by electroplating. If, for example, in the case of a vase, the decoration is to consist of a fine network of lines, the vase is completely enveloped with the paper (gummed on), and the lines are then cut out with a sharp knife. When a punch is used, the network is preferably cut beforehand, the paper being spread out flat, and afterwards carefully gummed on to the vase. Leaves, flowers, letters, etc., are cut with the punch first, and carefully finished off with a knife when the paper is in position.

It must be taken, as a rule, that all parts of the ware that are to be coated with metal must be fully exposed, this being done with great care, since there is no possibility of improving defective parts afterwards. If too much of the paper has been cut away in any place, this can be remedied by pasting another piece of paper and cutting the latter properly.

The prepared ware is next placed in a sand-blast machine, which, in the case of vases and other round ware, must be

arranged to turn on a vertical axis, so that all parts of the ware may be exposed to the blast.

The ware is left in the machine until the glaze has been completely removed from all the exposed portions, and the matt surface of unglazed porcelain is revealed. When expensive metals, like gold or silver, are to be employed, it is preferable to continue the action of the sand blast somewhat longer, so that the substance of the porcelain itself is etched away to a certain depth. By this means a thicker deposit of metal is obtained and the durability of the decoration is increased.

The next stage is to immerse the ware in water until the stencil paper comes away of itself and can be removed without difficulty.

Then the surfaces etched by the sand blast must be made electrically conductive. This can be done in various ways, one of them being to reduce pure graphite to an impalpable powder, by grinding and levigation, and then rub it firmly into the depressions in the ware by means of a fine brush. No particular care need be taken to confine this to the etched portions alone, the graphite being easily wiped off the smooth glazed parts with a soft cloth, though it adheres firmly to the remainder. This done, the ware must be carefully examined, bearing in mind that all portions of the surface that are to be coated with metal must show up black and shiny, *i.e.* be covered with graphite.

In a second method, all the etched portions of the ware are painted over carefully with a solution of silver nitrate, containing a little aniline dye, any portion of the nitrate that may have got on to the glazed parts being afterwards removed with a soft cloth. The piece is then placed under a bell glass, in which is inserted a small vessel containing aldehyde, the vapour of which reduces the nitrate to metallic silver, thus causing the coated parts to assume a silvery lustre.

This done, the piece is taken out of the bell glass, washed with a spray of water, and put in the electroplating bath. Any of

the metals that are deposited from solutions of their compounds by the electric current can be used for this class of decoration : platinum, gold, silver, copper (also brass or bronze), nickel, or cobalt. The bath liquor must, of course, contain the corresponding metal in a state of aqueous solution.

The ware being in the plating bath, the parts coated with graphite or silver must be connected with the source of current by a number of thin wires, which are coated with varnish except at the ends where they make contact with the silver or graphite. All isolated portions of the decoration must be connected up with the source of current in the same way, otherwise no deposition of metal will occur on them.

The bath is charged with the electroplating solution, and after any air bells on the coated portions of the ware have been carefully removed with a fine brush, the current is turned on, and allowed to act until the metal deposited on the coated parts projects a little beyond the surface of the glazed portions. The current is then turned off and the ware taken out of the bath, well rinsed and examined for any defects in the deposit, these being rectified by returning the ware to the bath.

The metallic deposit is always soft, and can therefore be pressed down by the burnisher, so that the surface is flush with that of the glaze ; at the same time it acquires a highly burnished lustre.

Designs in several metals can be applied by first plating in a bath of one metal, and then in one containing another metal, *e.g.*, decorating certain parts first with silver, and then others with gold.

Since ware decorated by this method must always belong to the class of expensive ware, owing to the time and cost expended in its production, the decoration is only applied to special, ornamental pieces, which, however, are certain to attract attention by their peculiar appearance, especially when the metallic decoration is tastefully combined with colour.

To produce a similar decorative effect at lower cost, it is advisable to first electroplate the etched portions of the surface with copper, and then coat the latter with a noble metal (gold or silver) in the same way. Of course, a portion of the copper can be faced with one metal, and other portions with another, an increased effect being obtained by producing a patina on some parts of the copper.

CHAPTER XI.

LUSTRE DECORATIONS ON PORCELAIN.

THE so-called lustre decoration affords a means of imparting a special appearance to porcelain ware. It may be divided into two chief classes : colourless and coloured lustre, the former comprising all those preparations by means of which the surface of porcelain is made to acquire a peculiar sheen which is not inherent in the glaze. Thus the sheen and gloss of mother-of-pearl or a moonlight effect can be produced by this means.

Coloured lustres impart a metallic lustre in addition to colour, the ware being made to acquire the appearance of oxidised bronze, for instance, or the iridescent effect of peacock feathers ; and peculiar colour and reflex effects can be produced by the conjoint use of colourless and coloured lustres.

In chemical composition, lustres are compounds of metallic oxides with the acids of ordinary pine resin, dissolved in a suitable solvent, lavender oil being usually employed for that purpose. These solutions are applied to the glazed ware and fired, whereupon the above-mentioned light and colour effects, which vary according to the lustre employed, appear direct.

The lustres may be prepared by two different methods : in the wet or the dry way. The wet method is preferable, as furnishing products of perfectly homogeneous composition, so that all parts of the ware are lustred alike when fired.

The usual method of preparation in the dry way is to carefully fuse the metallic oxides—preferably in the form

of nitrates—with pure pine resin in certain proportions, use being made of lavender oil to facilitate the combination of the metallic salts with the resin acids, and furnish direct a liquid which only needs suitable thinning down to be ready for use on the glazed porcelain ware.

Colourless lustres may be applied over colourless or coloured glazes, the sheen of the lustre in the latter case being modified by the underlying colour.

The colourless lustres are—

Alumina lustre,
Zinc oxide lustre,
Lead oxide lustre, and
Bismuth oxide lustre.

The coloured lustres include—

Iron lustre, which forms a lustrous red coating, which can be modified, by means of suitable adjuncts, into light brown or a golden tone.

Cadmium lustre.—This, when fired at a low temperature, gives a yellowish-red coating, which either does not appear at all at a high temperature, or, if formed, vanishes immediately.

Uranium lustre.—This handsome lustre has a peculiar greenish-yellow colour; and when mixed with bismuth lustre gives a mother-of-pearl sheen.

Nickel lustre when fired is a very agreeable light brown.

Cobalt lustre.—This varies in colour according to the degree of concentration used. In a very dilute state, the colour is chocolate brown, whilst more highly concentrated solutions give dark brown to nearly brownish black.

Copper lustre.—This has a peculiar reddish-brown colour.

Various additional effects can be obtained by mixing the above lustres in suitable proportions, an example of these being afforded by the so-called cantharides lustre and the metal lustres. These special lustres will be thoroughly described later.

PREPARING LUSTRES BY THE WET METHOD.

Though certain lustres can be prepared by the dry method, the majority are now made by the wet method, which will be described here in general, the only difference in the individual cases being in the metallic salts used.

The chief ingredient is a solution of sodium resinate or a soda-resin soap, obtained by preparing an aqueous solution of sodium carbonate, which is heated to boiling and treated with an addition of powdered pine resin (colophony) in successive small quantities. This resin mainly consists of acids which are sufficiently powerful to displace carbonic acid from combination as carbonates, and to combine with the metallic oxides forming the bases of these carbonates. In fact, a considerable frothing, due to the liberation of carbonic acid, will become manifest when the resin is thrown into the sodium carbonate solution. When the added resin no longer dissolves, this indicates that no more undecomposed carbonate is left, and that the solution contains nothing but dissolved sodium resinate.

The liquid, after being diluted with water, is boiled up again, and then left to settle until it has cooled down to ordinary temperature and all undissolved matters have subsided. The supernatant clear solution of soda-resin soap, which is pale yellow or light brown in colour, is decanted and is ready for use in the preparation of the various metallic resins.

With this object a salt of the desired metallic oxide is dissolved in water, diluted considerably and treated with a solution of resin soap so long as a precipitate continues to form. The precipitate is filtered off, washed with hot water and dried. It should be noted that only the alkali resinates are soluble in water, those of all the other metallic oxides being insoluble therein, and are consequently deposited as precipitates. Many of the resinates have the property of almost entirely losing

their solubility in ethereal oils on prolonged exposure to light. Consequently, the dried and finely powdered resins should always be stored in opaque vessels unless they are to be dissolved in ethereal oil at once.

PREPARING LUSTRES BY THE DRY METHOD.

To prepare lustres by the dry method, the usual plan is to melt resin in a porcelain basin at a moderate temperature and with constant stirring, and then stirring in the metallic salt until the latter has united completely with the resin. Since the mass assumes a viscous condition, it must be treated with a gradual addition of solvent (usually lavender oil), and warmed until a uniform solution is obtained.

The operation may be modified by dissolving the resin at once in the ethereal oil by the aid of warmth, and introducing the metallic salt into the solution. The colourless lustres, except the alumina lustre, which is always made by the wet process, are frequently prepared by the dry method.

Bismuth lustres are prepared by the dry method, by taking 10 parts of crystallised bismuth nitrate and 75 parts of lavender oil to 30 parts of resin. The latter is melted, heated slightly above its melting-point, and the bismuth nitrate is added in small portions, the mixture being energetically stirred after each. The mass soon begins to turn brown, whereupon the lavender oil is added in very small quantities at a time. When all this oil is in, the heating is stopped, and the covered vessel is left at rest, to allow the undissolved matters to settle down. The liquid is carefully decanted from the deposit—which can be used in the next operation—and is set on one side, protected from dust, until it has thickened sufficiently. This does not take long, lavender oil belonging to the class of ethereal oils which quickly resinify in the air.

The thickening can be accelerated by the aid of gentle heat, preferably in a shallow basin so as to present a large surface to

the air, and thus facilitate the absorption of oxygen by the lavender oil.

The same lustre can also be prepared in the dry way by triturating the finely powdered resin with the bismuth salt, also in a state of powder, the mixture being then melted, and the lavender oil added in small quantities.

Zinc lustre is usually prepared from zinc acetate, 1 part of this salt being melted with $2\frac{1}{2}$ parts of resin, and dissolved in lavender oil, in the warm.

Lead lustre is made from lead acetate, 1 part of which is melted with 3 parts of resin, and dissolved in lavender oil. When price is a consideration, lead lustre becomes very important, since it can be used in almost exactly the same manner as bismuth lustre, and is much cheaper.

The colourless lustres can also be readily prepared by the wet method, by dissolving the metallic salt in water, precipitating the solution with resin soap, and washing and drying the precipitate. The dried precipitate, being a very fine powder, readily dissolves in lavender oil. Bismuth lustre, however, is generally made as described above, the nitrate undergoing decomposition, with formation of the basic salt, when dissolved in water. In a certain sense the lustres of the noble metals also belong to the colourless class, the quantity of the contained noble metal being so small that its colour is masked by the peculiar light effect of the lustre. These lustres are often used in conjunction with colourless lustres, to produce additional effects.

When a lustre, dissolved in lavender oil, is applied on glazed porcelain, there remains, after the coating is dry, the resinate of the metallic oxide used ; or, when a lustre of a noble metal is in question, the peculiar organic sulphur compound of the metal existing in the balsam of sulphur.

On firing the lustre, the resinate is decomposed, leaving behind the exceedingly finely divided metallic oxide, which

readily fuses into the glaze owing to the addition of bismuth. The distribution of the oxide in the glaze produces the peculiar lustre effects, which cannot be obtained by any other means.

When a coloured lustre is mixed with one of a noble metal and fired, the latter is decomposed and the pure metal deposited, which, in conjunction with the coloured lustre, develops a new and often very beautiful series of light and colour effects.

NOBLE METAL LUSTRES.

The most beautiful lustre effects can be produced by the aid of bright gold, associated with bismuth lustre in suitable proportions. Since commercial bright gold is irregular in composition, and the effect of the gold lustre is intimately connected with the quantity of gold present, it becomes highly advisable to prepare the bright gold specially; and when this is done, in accordance with an invariable formula, a given quantity of the bright gold will always contain the same amount of metal and produce the same effect.

Five parts of bright gold and 1 part of bismuth lustre fired together on the ware give a coppery sheen; but if the proportions be changed to 2-3 parts of bismuth lustre to 1 of gold, the resulting colorations will be of a bluish-violet shade with a peculiar gold sheen. This effect can be graded in a uniform manner by modifying the amount of the bismuth lustre.

If the amount of the bright gold be increased, the blue passes through purple into rose colour, 2 parts of bright gold and 1 of bismuth lustre giving a beautiful rose red. On the other hand, 1 part of bright gold to 4 of bismuth lustre will furnish an agreeable pale blue.

These colour effects are apparently due to the varying distances between the individual gold molecules on the surface of the ware, according to the proportion of bright gold employed. This explains why the alteration in the quantities enables a whole series of effects to be obtained.

These colour effects can also be modified in various ways by adding to the bright gold and bismuth lustre certain quantities of other coloured lustres, such as those containing iron, chromium, uranium, etc. By experimenting largely in this direction, a way is opened to the ceramist of producing ware whose value is augmented by the novelty of its colour and lustre.

All the effects here mentioned can be obtained with ordinary bright gold, prepared as already described. Some makers, however, claim to obtain still finer results with a balsam of sulphur prepared from linseed oil. This balsam is easily made by heating 1 part of finely powdered sulphur with 3 parts of linseed oil until the frothing of the mass ceases and a quiescent black surface is observed, the whole being then diluted with oil of turpentine until the liquid can be strained through a not too closely woven cloth, after which it is mixed with a solution of gold chloride.

It should be specially mentioned that finely powdered sulphur—not flowers of sulphur—should alone be used, the latter always containing traces of sulphur dioxide that exert an injurious influence. If nothing but flowers of sulphur is available, these must be freed from sulphur dioxide by washing with water and subsequent drying.

Platinum lustre, which is frequently used instead of silver lustre, on account of its unalterability in air, whereas silver is soon tarnished, can be prepared in two ways: either by diluting bright platinum with lavender oil and nitrobenzol (obtainable in commerce as “oil of mirbane”), or by dissolving a saturated solution of platinum chloride in lavender oil. Except when the solution is too dilute, the platinum forms, after firing on the ware, a lustrous surface which completely covers the underlying glaze.

Silver lustre is obtained by mixing silver nitrate with lavender oil, and firing the ware in a reducing atmosphere, the

silver being reduced to the metallic state and forming a bright coating. A peculiar sheen can be imparted to the silvered surface by applying a very dilute solution of gold.

THE RESINATES OR RESIN SOAPS.

The technical papers frequently contain recipes for producing specially fine lustres; but these do not always give the desired results. The following, however, can be relied on.

The resin soaps for this purpose are prepared in a somewhat different manner from that already described, caustic soda being used in place of the carbonate.

Five hundred parts of powdered pine resin are heated with 300 parts of caustic soda lye (2 parts of water to 1 of caustic soda). The mixture is stirred continually until all the resin has dissolved, a yellow mass being obtained on cooling. This is broken into small pieces and washed for a short time with water, which turns brown and is poured away. The finished soap is then dried, and can be used at once for the preparation of resinates, according to the subjoined formulæ.

Iron Resinate.

Resin soap, 1000 parts, and water, 2000 parts, are dissolved by heat, and an aqueous solution of 350 parts of ferric chloride is stirred in, the resulting brown precipitate of iron resinate being washed and dried slowly. All the other resinates mentioned below are prepared in the same manner.

Uranium Resinate.

Resin soap, 1000 parts, dissolved in water, 2000 parts.
Uranium nitrate, 500 parts.

Chromium Resinate.

Resin soap, 1000 parts; water, 2000 parts.
Chrome alum, 500 parts.

Manganese Resinate.

Resin soap, 1000 parts ; water, 2000.
Manganous sulphate, 500.

Copper Resinate.

Resin soap, 1000 parts ; water, 2000.
Copper sulphate, 500 parts.

Lead Resinate.

Resin soap, 1000 parts ; water, 2000.
Lead acetate, 600 parts.

Bismuth Resinate.

This resinate, which cannot be prepared with resin soap as described above, is obtained by melting 1000 parts of pale resin (colophony) and mixing with this 300 parts of basic bismuth nitrate. When the effervescence has subsided and the mass is quiescent, 1500 parts of lavender oil (or a mixture of this and nitrobenzol) are gradually added, and the liquid is left for any insoluble matter to settle down. The lavender oil may be replaced by rosemary oil, or by a mixture of lavender oil, rosemary oil, and oil of turpentine.

To dissolve the resinsates prepared in the foregoing manner, they must be stirred with the solvent, in the warm, until complete solution has apparently been obtained. Warming is then continued, without stirring, for some time, to allow the insoluble matter to settle down, after which the clear solution is carefully decanted from the sediment. Lavender oil, rosemary oil, and benzol are the solvents used.

Iron Solution.

Iron resinate, 1000 parts.
Rosemary oil, 2000 parts.

Uranium Solution.

Uranium resinate, 1000 parts.
Benzol, 300.
Rosemary oil, 2000 parts.

Chromium Solution.

Chromium resinate, 1000 parts.
Rosemary oil, 3000 parts.

Manganese Solution.

Manganese resinate, 1000 parts.
Benzol, 300.
Rosemary oil, 2000 parts.

Cobalt Solution.

Cobalt resinate, 1000 parts.
Rosemary oil, 2000 parts.

Copper Solution.

Copper resinate, 1000 parts.
Rosemary oil, 2000 parts.

Lead Solution.

Lead resinate, 1000 parts.
Benzol, 300.
Rosemary oil, 2000 parts.

Tin Solution.

Thirty-two parts of tin salt (stannous chloride) are dissolved in 100 parts of ether, the solution being then stirred vigorously in the cold, with 90 parts of balsam of sulphur, of the composition given below, and gently heated until all the ether has evaporated. Stronger heat is next applied, and a mixture of 3 parts of clove oil, 1 of nitrobenzol, and 6 of lavender oil is then well stirred in, enough being used to make the total mass

up to 340 parts. The solution must be left to stand some time before use, to allow the undissolved matter to subside.

BALSAM OF SULPHUR.

Powdered sulphur	300 parts.
Venice turpentine	80 „
Oil of turpentine	70 „

This mixture is heated until brown fumes begin to come off, whereupon a further 150 parts of Venice turpentine and 600 of oil of turpentine are added, the heating being continued. The cooled mass should remain clear and transparent, turbidity indicating that the sulphur has not all been dissolved, and that the mass must be reheated with a further addition of turpentine and oil of turpentine.

RECIPES FOR PREPARING LUSTRES READY FOR USE.

White Lustre, No. 1.

This consists of the bismuth resinate solution prepared as above.

Brilliant Lustre, No. 2.

Colophony, 500 parts ; basic bismuth nitrate, 100 ; rosemary oil, 500 parts.

White Lustre with Tin, No. 3.

Tin solution, 1 part ; white lustre, No. 1, 3 parts.

Yellow Lustre, No. 4.

Uranium solution, 3 parts ; white lustre, No. 1, 1 part.

Yellow Lustre, No. 5.

Uranium solution, 9 parts ; lead solution, 1, white lustre ; No. 1, 2 parts.

Lemon Yellow Lustre, No. 6.

Chromium solution, 1 part ; brilliant lustre, No. 2, 3 parts.

Bronze Lustre, No. 7.

Chromium Solution, 1 part ; lead solution, 3 parts.

Iron Red Lustre, No. 8.

Iron solution, 3 parts ; white lustre, No. 1, 1 part.

Yellow Brown Lustre, No. 9.

Iron red lustre, No. 8, 5 parts ; yellow lustre, No. 4, 2 parts.

Chamois Lustre, No. 10.

Iron red lustre, No. 8, 3 parts ; white lustre, No. 1, 12 parts.

Pink Lustre, No. 11.

Bright gold, 1 part ; white lustre, No. 1, 5 parts.

Purple Lustre, No. 12.

Bright gold, 1 part ; white lustre, No. 1, 5 parts.

Gold Lustre, No. 13.

Bright gold, 1 part ; white lustre, No. 1, 3 parts.

Yellow Green Lustre, No. 14.

Bright gold, 1 part ; white lustre, No. 1, 10 ; yellow lustre, No. 5, 30 parts.

Dark Green Lustre, No. 15.

Bright gold, 1 part ; white lustre, No. 1, 6 ; yellow lustre, No. 5, 12 parts.

Blue Lustre, No. 16.

Bright gold, 2 parts ; tin solution, 5 ; white lustre, No. 1, 20 parts.

Blue-Green Lustre, No. 17.

Yellow lustre, No. 13, 2 parts ; Yellow-green lustre, No. 14, 1 part.

Steel Green Lustre, No. 18.

Pink lustre, No. 11, 26 parts ; iron-red lustre, No. 8, 26 ; gold lustre, No. 13, 32 parts.

Grey Lustre, No. 19.

Pink lustre, No. 11, 1 part ; tin solution, 1 ; white lustre, No. 1, 4 parts.

Grey Lustre, No. 20.

Cobalt solution, 1 part ; white lustre, No. 1, 3 parts.

Grey-Brown Lustre, No. 21.

Manganese solution, 3 parts ; white lustre, No. 1, 1 part.

Brown Lustre, No. 22.

Iron red lustre, No. 8, 9 parts ; bright platinum, 1 ; dark green lustre, No. 15, 1 part.

Dark Brown Lustre, No. 23.

Iron red lustre, No. 8, 5 parts ; bright platinum, 2 parts.

Bronze Lustre, No. 24.

Bright gold, 1 part ; brilliant lustre, No. 2, 1 ; iron solution, 1 part.

Bronze Lustre, No. 25.

Bright gold, 1 part ; manganese solution, 1 ; brilliant lustre, No. 2, 1 part.

Bronze Lustre, No. 26.

Bright gold, 2 parts ; cobalt solution, 2 ; brilliant lustre, No. 2, 1 part.

Bronze Lustre, No. 27.

Bright gold, 1 part ; yellow lustre, No. 5, 1 part.

Bright Silver, No. 28.

Bright gold, 1 part ; bright platinum, 2 parts.

As a rule the lustres are thicker than is necessary, and are therefore diluted with lavender oil, as required, for use. Should, however, a lustre be so thin as to flow beyond the desired limits when applied to the ware, this defect is remedied by adding a sufficiency of a thick solution of resin in lavender oil.

When large surfaces are to be coated with lustre, the latter must not be either thinned down or thickened during the progress of the work, or the lustreing will come out uneven and irregular.

SPECIAL LUSTRES.

Apart from the numerous combinations that can be prepared by mixing the foregoing lustres in varying proportions, there are certain effects that can only be obtained by special means, notably certain red lustres, prepared with gold, and the so-called cantharides lustre.

RED LUSTRES.

These, also known as 'Burgos' lustres, are distinguished by a peculiar red sheen, and are translucent. Though their preparation is stated by some makers to be a secret, they can be easily made by selecting a gold lustre of suitable red colour and mixing this with colourless bismuth lustre in suitable proportions.

When the properly made lustre is applied to a colourless glaze, it merely shows a red colour, whereas with a coloured glaze that harmonises with the lustre, very rich and handsome colour effects are produced. For example, a blue glaze, not

too deep in colour, will produce a peculiar purplish sheen, whilst a yellow glaze will give orange tones, etc.

According to Zsigmondy's patent specification, rose red, deep red, and also purple lustres are obtained by proceeding in the following manner:—

Commercial gold sulpho-resinate solutions, such as are used for bright gold, are treated with solutions of organic compounds of silica. The proportion of gold and silica in the mixture depends on the colour to be produced, and ranges between 0·7 and 5 parts of silica to each 1 part of metallic gold. The lower the proportion of silica, the darker will the shade of the colour when fired. The addition of white bismuth lustre imparts a violet tinge, the colour being no longer pure red.

A silicon compound suitable for this purpose can be prepared by mixing alcohol, ethereal oils, or resin solutions with silicon chloride, and waiting until the reaction, which is accompanied by the liberation of hydrochloric acid gas, is complete. The surplus silicon chloride is expelled by heat and is mixed with the gold solution in the right proportion for producing the desired shade of colour.

Also according to Zsigmondy, ruby, yellow-red, and yellowish rose red lustres can be obtained by heating 3 parts of colophony and 30 of sulphur to 270° C., dissolving the mass in 70 parts of absolute alcohol, and heating this solution with one consisting of 5 parts of silver nitrate and 6 parts of water for half an hour on the water bath. The whole is then poured into a large volume of water, whereupon the silver sulpho-resinate separates out. This is dissolved in lavender oil, and is mixed immediately before use with the aforesaid siliceous gold sulpho-resinate mixture.

CANTHARIDES LUSTRE.

The wing cases of numerous beetles exhibit a peculiar gold lustre, combined with a blue or green coloration. This pheno-

menon is beautifully exemplified by the rosechafer, and still more particularly by the elytræ of the cantharides beetle or Spanish fly, *Lytta vespicatoria*.

Cantharides lustre is a yellow lustre, which is chiefly applied to blue glaze, in conjunction with which it furnishes a peculiar green metallic sheen. This lustre is prepared by applying a lead glaze with a small quantity of bismuth oxide and pure silver chloride, and firing it on the ware in muffles containing a reducing atmosphere. Under these conditions a portion of the silver chloride and of the lead glaze is reduced, and the fired coating exhibits all the colours of the rainbow. To obtain a fairly uniform coating of the lustre it is essential that the ingredients should be evenly applied, and that the reduction should not take place until the ware is at full red heat.

Various colour effects are obtained by modifying the mixed lustres; thus, 5 parts of bismuth lustre and 1 of chromium lustre, for instance, will give a yellowish sheen, whilst equal parts of lead and chromium lustres furnish orange red.

Suitable admixtures of the said lustres with zinc, alumina and cobalt lustres will give green and greenish-blue to blue lustres, according to the amount of cobalt lustre employed.

The application of the lustre preparations to the ware entails a certain amount of skill on the part of the operator, it being necessary to coat the glaze evenly in order to obtain a uniform result. If a portion of the glaze, that has already been coated with lustre and is fairly dry be gone over again, it will show up much brighter or darker coloured (in the case of coloured lustres) than the rest when fired.

This peculiarity may be utilised, in decorating vases for instance, by applying more coatings to the upper portion than the lower part, so as to produce a certain gradation and cause the top portion to show up darkest in colour, the depth

decreasing progressively downward, the part that has received only a single coating being the lightest.

When it is desired to apply several different coloured lustres, so that the shades shall merge into one another, the second lustre is applied before the first one is perfectly dry, the two flowing together at the lines of contact and thus forming beautifully coloured transition stages. If the first lustre be a blue and the second a yellow, a green will be formed at the parts in question, shading off into blue at the edges. A red lustre topped with a yellow will give orange in the same way, and so on.

CHAPTER XII.

FIRING MUFFLE COLOURS.

THE firing, or more properly fusing, of muffle colours is performed in special appliances known as muffles. The object of firing the colours is to fuse the flux, which is intimately incorporated with the actual colouring matters. At the same time, the flux and glaze on the ware fuse together, so that when cold the flux envelops the colour in the form of a colourless glaze.

THE MUFFLE.

Whatever the arrangement of the muffle, it must always fulfil the condition that the internal space in which the ware is placed is shut off from all access by the furnace gases. Apart from the fact that these gases often contain small particles of ash or unconsumed fuel, they not infrequently consist of a gaseous mixture of strongly reducing properties, and might therefore entirely change the colours if allowed to come in contact with them at high temperature, thus spoiling a valuable decoration.

To entirely preclude this danger, each muffle must be so arranged that it can be completely shut up, with the exception of very narrow openings through which the expanded hot air from within can escape, and afterwards return while the muffle is cooling down. A small lateral pipe must be provided through which the progress of the firing can be observed, in order to ascertain when the colour has been sufficiently fired, the ware

being placed in such a position that this inspection can be made through the pipe.

It was formerly the practice to place each muffle in a separate furnace, and allow the flame to surround it on all sides except the front, this side being closed by a properly fitting cover. The furnace, with the enclosed muffle, had to be left untouched after the firing process, until it had cooled down to the ordinary temperature, since any sudden cooling might easily crack the ware.

Owing to the waste of time involved in using this class of muffle furnace, it has now been abandoned in all large potteries, and replaced by a type that enables the work to be carried on continuously. Apart from the saving of time, this new type of muffle furnace offers the advantage of consuming less fuel than the older form in which the whole furnace had to be heated afresh with every charge. This continuous type of muffle furnace will be more fully described later on.

It should, however, be noted that every work is provided with a furnace holding only a single muffle, so as to be able to fire single pieces of special size. For instance, expensive porcelain vases, decorated in colours by artists, will not be fired in a large muffle along with inferior ware, but always in a muffle by themselves.

The simplest arrangement of a muffle and its furnace is shown in Fig. 19. The muffle M has the shape of a round topped box, and is made of fireclay. It is placed in a furnace O, so arranged that the furnace gases ascending from the grate R can surround the muffle on all sides, and heat it to a uniform white heat all over. A fireclay plate P, mounted in front of the muffle, enables the pieces to be fired to be easily inserted and withdrawn. Each muffle is also provided with a plate of the proper shape for closing the front end.

For tall, slender vases and other ware whose height considerably exceeds the diameter, muffles of corresponding shape must

be used, and these must be mounted in furnaces of suitable dimensions. It being difficult to make such muffles in a single piece, they are always built up of a number of smaller plates, as will be described later on.

It should be noted that muffles arranged as mentioned above are rarely used in large works for firing a number of pieces at a time, though they are well adapted for treating small pieces requiring special care in firing. The most usual

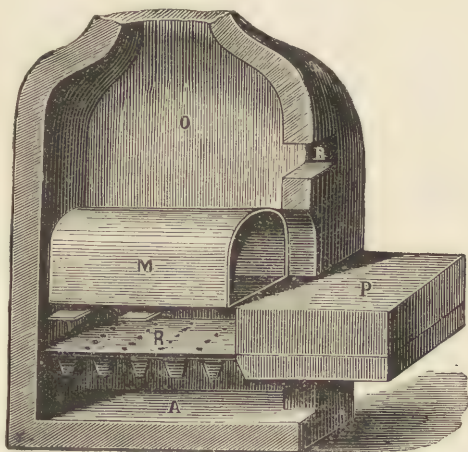


FIG. 19.

form of muffle for firing muffle colours on porcelain differs somewhat in arrangement from that already described. The disposition of the ordinary muffle for firing porcelain colours can be seen from Figs. 20 and 21.

In Fig. 20, the muffle M is made of stout sheet brass, mounted in a clay lined iron casing, and so small that only a small plate or a few coffee cups can be fired at a time. As shown in the drawing, the muffle is fitted for heating by two or more spirit lamps.

The muffle shown in Fig. 21 is intended for use in large works. Here, again, the muffle M is a prismatic fireclay box, made in one piece, and left open at the front end for the introduction of the ware, a fireclay coverplate being inserted in the opening when the muffle has been charged. In the middle of the plate is a horizontal tube, for inspecting the progress

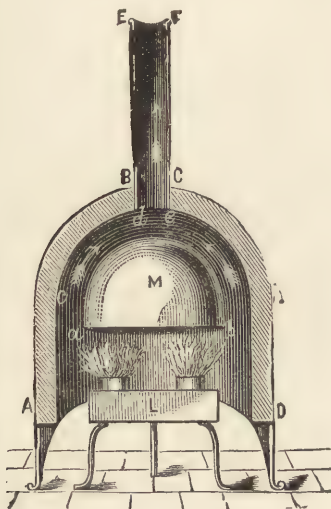


FIG. 20.

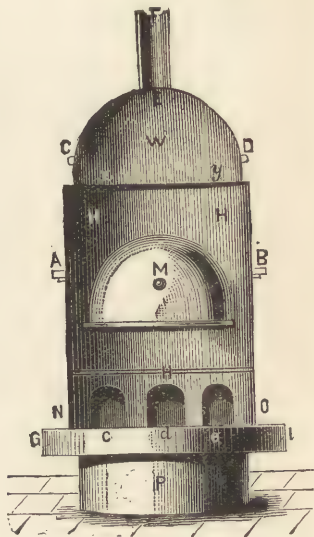


FIG. 21.

of the ware in course of being fired, which tube is closed with a cap of sheet metal, except when the inspection is being made, at which time the cap is replaced by a ring enclosing a piece of glass or colourless mica to protect the eye from the hot gases flowing out of the muffle. On the top of the dome at E is mounted a narrow tube, to allow the expanded hot air to escape, and also to conduct away the vapours liberated by the volatile oils used in applying the colours.

The arrangement of the furnace itself is a very simple one. The muffle is inserted in such a way that it is supported by three or more arches, *c, d, e*; and the side walls of the furnace are so close to the muffle that the latter is always laved by the furnace gases. In Fig. 21 the firing is arranged so that fuel is introduced at the side next the open end of the muffle.

As will be easily imagined, however, it is preferable to provide the opening for the fuel on the opposite side, *i.e.*, that next the rear end of the muffle, this preventing the access of smoke, coal-dust, etc., into the muffle itself.

Though muffles of unglazed fireclay can be used, it is sometimes advisable to glaze them inside, to make them gas-tight and more durable. For this purpose it is usual to employ a far more refractory glaze than the colours to be fired in the muffle; which glaze must be fused before the muffle is employed.

This is effected by heating the muffle very gradually to redness, then raising it to a temperature sufficient to flow the glaze, after which the furnace is allowed to cool down, this being necessary to lessen the risk of the muffle cracking the first time it is used.

Sooner or later, however, all muffles will crack at the sides; and every endeavour must be made to repair them as effectually as possible, to avoid having to discard the muffle as useless and replace it by a new one. In doing this it is not advisable to merely stop the cracks with fireclay, since this will shrink and leave the muffle leaky again. The better plan is to paint the cracks over with the same glaze as used inside the muffle, and to mix about 5 per cent. of this glaze with the fireclay with which the cracks are repaired. The next time the muffle is strongly heated, this glaze will fuse and stop up the cracks completely.

When, finally, the muffle is worn to such an extent that it does not seem capable of being repaired any more, it must be

replaced by a new one—a somewhat expensive matter, and also entailing the removal of the whole front of the furnace.

For this reason it is preferable not to make the muffle all in one piece, but to build it up of a number of small hollow fireclay plates carefully cemented together with fireclay mortar so as to make the joints as tight as possible. When finished, the entire inner surface of the muffle, especially at the joints, is thickly coated with glaze, which is then fused.

When a muffle of this kind gets damaged, the injury is usually confined to individual plates, which are then broken out and replaced by new ones, which are afterwards glazed.

So far as the heating of the muffle is concerned, a very practical arrangement has been adopted of completely separating the furnace fire from the muffle, the gases being conducted through flues so as to surround the muffle and then pass away through a conduit underneath the latter to a chimney of sufficient height to create the necessary draught.

In charging the muffle with ware, the whole of the internal space should be utilised as completely as possible. Consequently the bottom of the muffle should be covered with pieces of equal height, between which are set fireclay supports for upholding fireclay plates to carry smaller pieces.

When the muffle has been charged and the front plate set in position, the firing is commenced. At first the heat is applied gently, in order to warm the muffle and charge right through; but as soon as this condition is reached, the heat is increased to a temperature sufficient to fuse the flux in the colours. When inspection through the peephole has shown that the colours are properly fired, the fire is either put out or drawn, and the muffle left to cool.

Owing to the constant liability of the muffle to crack and admit the furnace gases, firing in ordinary muffles is always a matter of chance, and it is therefore better to minimise this risk by doing away with direct fire heat and using the furnace

gases from a regenerator, connected with several muffles by flues and dampers. If three muffles, for instance, are mounted together, the gases are first passed under the first muffle until this is sufficiently heated, the waste gases (still very hot) being led under the second and third muffles so as to warm their contents. As soon as the finishing heat in the first muffle is attained, the damper is closed, and the gases admitted under the second muffle direct. The third muffle is treated in the same way; and when this is heated to the proper temperature, the gases are led under the first muffle of a second set, and so on.

Within a short time, the first of the muffles will have cooled down enough for the front plate to be removed and the ware taken out; this being also the case with the second and third muffles in turn. When all three have been emptied and refilled with fresh charges of ware, the firing can be recommenced in the same way as before; and in this way the work can be carried on continuously, thus reducing the consumption of fuel to a minimum.

DRAUGHT MUFFLES.

When inferior ware and small pieces (coffee cups, dolls' heads, pipes, etc.) have to be fired, use is frequently made of draught muffles, which are also arranged to ensure continuous working. The arrangement is as follows: the muffle is open in front and is surmounted by a second muffle open at both ends. The furnace gases pass round the bottom muffle first, and then the upper one, from which they pass into a long flue, which has also double walls, so that its interior has the same section as the muffle, and this is heated by the surrounding furnace gases. This heating is greatest immediately under the upper muffle, and gradually diminishes rearward, so that the portions of the flue farthest away from the muffle are heated the least.

The ware to be fired is supported by iron plates with slightly turned-up edges. Porcelain pipes, and other pieces, that cannot be supported in this way, are mounted on iron studs projecting from the plates.

A plate laden with ware is inserted at the back of the flue, and after a certain time is followed by a second one, which pushes the first one forward. This is repeated, the first plate thus constantly advancing into a hotter portion of the flue until it finally reaches the upper, glowing muffle, which serves as a preliminary heater.

At this stage the plate is gripped by a pair of tongs and transferred from the upper to the lower muffle, where the firing of the ware is accomplished. Owing to the high temperature already attained, the actual firing takes only a very short time: and as soon as it is over, the plates are taken out of the muffle and set on one side, the next plate in the series being transferred to the finishing muffle, and the work carried on continuously in this manner as long as desired.

At the very high temperature at which the ware leaves the muffle, it is very liable to crack by sudden cooling; and it is therefore advisable to place the loaded plates in a conduit arranged in exactly the same way as the one for heating the ware but in reversed order, the part next the muffle being the hottest, and those more remote progressively cooler. In this way the ware is gradually cooled to such an extent that on being withdrawn at the farther end, there is no risk of it cracking.

Instead of employing two conduits, one for introducing the ware to, and the other for withdrawing it from, the muffle, the whole series of operations may be performed in a single conduit or tunnel.

TUNNEL MUFFLE FURNACES.

These furnaces derive their name from their resemblance to a tunnel, the fireclay pipes composing the conduit having

a similar section. The fireplace is at the central portion of the tunnel, and the furnace gases produced therein are conducted round the latter in both directions.

When the plates or trays charged with ware to be fired are introduced at the one end of the tunnel, they are pushed forward by the succeeding trays, and finally arrive at the hottest central portion of the tunnel. Here they remain until the firing is completed, and are then pushed forward again, in the same manner as before, through successively cooler portions of the tunnel, and on issuing at the farther end are cool enough to preclude risk of cracking the ware.

The hottest portion of the tunnel may be provided with a couple of peepholes covered with colourless mica plates, to enable the appearance of the fired ware to be observed, and to ascertain how long it is necessary for the ware to remain there before it can be regarded as finished. With a little experience, this inspection becomes superfluous, and the forward movement of the trays is effected at predetermined intervals.

A number of methods and appliances for shortening the length of the tunnel, which is considerable, have been proposed. In one instance the length has been reduced one-half, by making the tunnel wider and dividing it into feed and return portions by a thin longitudinal partition, the actual muffle being at one end of the double tunnel and of the same width as the latter.

In working with this modification, the iron crates containing the charges of ware are inserted successively into the feed tunnel, the ware becoming progressively hotter as they advance toward the muffle. When the first crate reaches the muffle, it is left there until the glaze has melted on the ware, and is then pushed aside into position for entering the return tunnel. Through this it is moved forward by the succeeding crates until it issues from the mouth of the tunnel and is taken away.

Various means have been proposed for obviating the difficulty experienced in pushing the heavy crates over the floor of the tunnel, the simplest being to lay a rail track on the bottom of each tunnel and mount the crates on wheels. This enables the crates to be moved with a minimum of friction and motive power.

When, as in the present instance, the two tunnels are side by side, a pair of small turn-tables must be provided in the muffle, to enable the crates to be transferred from one rail track to the other.

The feed tunnel may also be given a slight downward slant, so that the crate trucks run forward to the muffle by gravitation, and are retained there by a simple brake mechanism. Similarly, the return tunnel has also a slight gradient, but in the opposite direction, so that the trucks tend to run out of their own accord.

When the crates are mounted on wheel trucks with a certain amount of play to the wheels, and both feed and return tunnels are laid with rail tracks, the whole installation can be arranged in the form of an incomplete ring, with the fireplace in the centre of the arc. In such case the crates of ware, after getting hotter and hotter and being fired in the muffle, then become progressively cooler in the cooling tunnel, and issue from the latter close to the original point of entry.

It is always advisable to have both tunnels fairly long, owing to the more gradual heating and cooling than is possible with shorter tunnels, and the resulting increased security against cracking. In this connection earthenware is more susceptible to damage than porcelain, and with short tunnels the percentage of loss by cracking is considerable, whereas with long tunnels it is inappreciable even in the case of common ware.

Where long tunnels are used it is important that the furnace gases should flow round the tunnels with the requisite velocity,

the muffle being provided with a powerful draught for that purpose. The heat that would otherwise be wasted owing to the rapid flow of the gases, is utilised by passing the gases through a system of heating pipes in the drying room on their way to the chimney-stack, thus preventing a waste of fuel.

MUFFLE FURNACES FOR SPECIAL PURPOSES.

For certain purposes it is desirable to modify the arrangement of the muffle accordingly, more particularly when portions of partially finished ware have to be decorated with another colour or with metal, or when small articles not made on a large scale are to be fired. Some photographers make the production of indestructible photographs on porcelain a part of their business, and these, of course, are only made in a small number of pieces at a time, so that specially arranged small muffles, usually heated with gas or by methylated spirit, are required (see Fig. 20).

Fig. 22 illustrates a furnace arranged for heating by gas on the Fletcher system. Coal-gas is supplied through a large pipe in the lower part of the furnace, and, becoming mixed with air during its ascent, burns with a blue flame surrounding the muffle M when lighted. These gas muffles get so hot that the firing of the ware takes only a very short time. This is especially the case when the muffle is once hot, a large number of small articles being then handled very quickly.

These small gas muffles are also very suitable for touching up finished ware, the defective colours or glaze being removed in the sand-blast machine and made good by a fresh application, which is then fired in the gas muffle. In this way it is possible for ware that has entailed a great deal of labour to be saved from relegation to the class of outshots, as the consequence of some slight defect, and restore it to good condition.

There is of late a growing tendency to apply gas heating to

large muffle furnaces as well, the gas being produced in a special generator.

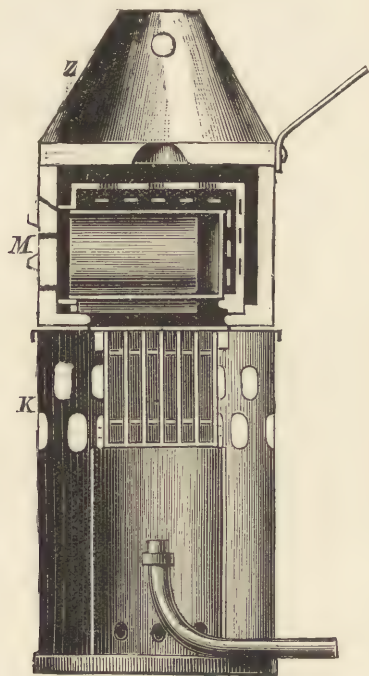


FIG. 22.

THE APPLICATION OF GAS FIRING IN CERAMICS

The numerous inconveniencies attending the application of direct fire heat in the production of ceramic ware—more especially fine ware, such as porcelain or faience—are only too well known to all ceramists. It may be asserted with all confidence that a very large proportion of the wasters found on inspecting the finished ware is due to this method of firing.

Two circumstances in particular have to be considered in this

connection. One is the great difficulty experienced, despite all precautions, in excluding ash and coal dust from the furnace gases. Although all fine ware is protected in the kiln by being enclosed in saggars, the dust cannot be entirely kept out of these coverings in the event of their cracking or becoming imperfectly closed.

Since the ash of fuel always contains particles of ferric oxide, both biscuit and glazed ware are liable to become spotted in the kiln, and reduced in consequence to a lower grade or to the condition of wasters.

Almost equally injurious is the presence of reducing gases, which becomes specially manifest when colours are being fired on the ware. It has already been pointed out that a large number of the ceramic colours contain metallic compounds that undergo considerable alteration by the action of reducing substances, the colours being either of a different shade to that desired or quite another colour altogether.

Now, since the firing process is the final link in the long chain of operations leading from the raw clay to the finished ware, the losses caused to the manufacturer are very severe when the colour is spoiled in firing, comprising, as they do, not only the loss of the valuable material, but also the waste of expensive labour bestowed in making the spoiled ware.

Attempts have been made to counteract the appearance of these reducing gases by the introduction of an increased supply of air beyond that necessary for the complete combustion of the fuel. But, without affording a perfect remedy, this method leads to an increased consumption of fuel, owing to the large amount of nitrogen ($\frac{1}{3}$ ths) present in the air and having to be heated with it, the rapid velocity of the escaping gases also preventing the complete utilisation of the contained heat for the purpose in view, namely, the firing of the ware, glaze or colour.

A measurement of the temperature of the gases escaping into the chimney-stack will afford convincing proof that the greater part of the heat generated in the furnace is being wasted.

The first endeavour to remedy this unpleasant state of things was made early in the nineteenth century, but quite fifty years' labour was required to bring it to perfection. The first instigation to these researches was on the part of makers of wrought and cast iron and steel, in order to utilise for heating purposes the enormous quantities of heat wasted in the blast furnace. After long and careful experiment very successful results were obtained, and these attracted the attention of all concerned with methods of heating. The idea involved was to construct furnaces capable of consuming poor fuel, like inferior lignite and coal-dust, so completely that the furnace gases should contain no combustible ingredients, and therefore no reducing substances, the gases at the same time being entirely free from dust. The object in view, therefore, was the production of completely consumed glowing gases.

The final results of these experiments are embodied in the installations grouped under the name "generator furnaces," or "gas generators." A description of this class of plant is beyond the scope of the present work ; and readers desiring information on the matter are referred to the numerous technical works dealing with the subject, all that we can do here being to summarise the principle on which these generators are constructed.

The fuel used—which, as already mentioned, may be very inferior coal—is burned in a shaft furnace, the combustion proceeding from below upward, so that the products have to ascend through an overlying layer of the fuel, which is subjected to a process of dry distillation by their heat, *i.e.* disengages combustible gases and vapours. The shaft furnace is tightly closed at the top, and is fitted with a charging device through which the fuel can be introduced without admitting air.

The combustible gases and vapours are supplied, by means of special devices, with just sufficient air to support their complete combustion. Theoretically, the glowing gases will then contain

only carbon dioxide, water vapour, and nitrogen, and the temperature of the current of gas is at its highest possible point. The gases are then conveyed through suitable pipes or flues, to the places where their contained heat is to be utilised for smelting metals, firing ware, etc.

A further advance has been made by connecting the generator furnace with a contrivance for storing up the contained heat of the gases to a certain extent, and enabling this heat to be drawn upon when required. These heat accumulators consist principally of chambers with very thick walls, which retard the radiation of the heat as much as possible, the internal space being filled with chequerwork so as to compel the gases to take the longest possible course on their way to the stack, meanwhile parting with their heat to the chequerwork, which is thereby raised to a very high temperature.

The time required for the accumulator to be heated to its fullest capacity depends on the size of the furnace and of the chamber, and must be ascertained in each case by experiment. If, when this point is reached, the supply of furnace gas is cut off, a current of air can be passed through the accumulator, and absorbs heat from the brickwork, thus becoming converted into a source of heat itself. After a certain time, however, the brickwork will be cooled down below the requisite temperature, whereupon the air supply must be cut off and the chamber heated up again as before.

To prevent the loss of time entailed by this interruption of the process, the accumulator must be duplicated, so as to work continuously, one chamber being heated whilst the other is being used for heating the air current, each chamber thus serving in turn.

By the provision of suitable conduits and valves, the diversion of the currents of gas and air between the accumulators can be effected almost instantaneously, the process working uninterruptedly as long as the furnace is in operation. In large plants several of these furnaces can be provided.

There will be no difficulty in realising the enormous advantages that can be derived from the application of this system of heating in all industries requiring the use of high temperatures, more especially in ceramic works, since it furnishes a current of gas of any desired strength and temperature, perfectly free from ash and any admixture of reducing substances (the combustion of the gases being complete). To raise or lower the temperature of the space in which the gases are to part with their heat, all that is necessary is to regulate the damper controlling the flow of gas.

In installing a ceramic works for gas firing, the arrangement of the various details of construction is to some extent self-evident, the chambers, for instance, in which the highest temperatures are to be produced, being necessarily placed as near as possible to the heat accumulator. The gases issuing from these chambers must be conducted direct into those requiring a somewhat lower, but still high, temperature, such as for fusing glazes. By passing the hot gases gradually from chamber to chamber they part with their heat by degrees, and can finally be utilised for heating the drying-rooms for the green ware, materials, etc., before escaping into the stack. The fuel, or the heat furnished thereby, is thus completely utilised to an extent impossible by any other system, and gas firing must therefore be regarded as the most economical of known methods.

We have now briefly sketched the advantages resulting from gas firing in general, and for the ceramist in particular. They are so clearly apparent that one may rightly claim that no ceramic works can be considered as up to date unless equipped with gas-firing plant. So great, indeed, are the benefits derived from the system that the high prime cost of the installation is soon recouped and the investment repaid with interest.

CHAPTER XIII.

THE IMITATION OF PAINTINGS ON PORCELAIN.

EXTENSIVE use has latterly been made of a special process for imparting to ceramic ware the appearance of painted porcelain (including decoration with metals), since it enables articles barely distinguishable from the finest painted porcelain, to be produced at comparatively cheap prices.

SIDEROLITH.

The ware obtained by this process is known as "siderolith" (meaning ironstone) or "terralith" (earth stone). The body of the ware consists of any white or coloured clay that has been properly prepared and possesses a high degree of plasticity. According to the amount of iron in the clay, the biscuit ware is more or less red or yellow in colour; and being porous it will adhere firmly to the tongue.

The glazes and colours applied to this ware, however, are ordinary oil paints, applied with the brush or by means of transfers.

The making of the ware proceeds on exactly the same lines as for fine porcelain, the pieces being usually cast in plaster moulds, and carefully dried at a moderate temperature, this being the best way to prevent loss by distortion. The properly dried ware is then fired at moderate kiln heat and handed over to the painter. Ordinary oil colours are employed for this class of ware; and as the finished pieces are not sub-

jected to any high temperature, organic colouring matters can be used.

The colours are prepared by triturating the finely powdered pigments with oil of turpentine, and adding enough finest amber varnish or copal oil varnish to make the colour workable, and furnish, when applied with the brush and dried, a uniform, lustrous coating that will retain its beauty for a considerable time without losing its fine gloss. Should the glass fade in a short time, it will be certain to disappear entirely in a few months. This defect is due to the varnish in the colour drying too quickly and shrinking, thus forming a number of extremely fine cracks in the colour. These cracks, though invisible to the unaided eye, destroy the cohesion of the colour so that it no longer reflects light uniformly, and therefore has a matt appearance.

One of the causes operating in this phenomenon is the use of too high a temperature in drying the painted ware, the varnish not having sufficient time to contract gradually; whilst on the other hand the nature of the varnish itself may cause the layer of colour to crack.

Oil varnish deficient in oil shrinks irregularly in drying, and therefore easily cracks. This defect can be remedied by adding more boiled oil to the copal or amber varnish, or adding a small quantity of a soft-resin varnish, such as dammer varnish, or a very little castor-oil.

The interior of vases, jugs, etc., and the under side of dishes or plates will usually be coated with a uniform layer of colour. Zinc white is preferably used for white, chrome green for green, and so forth; but owing to the difficulties thrown in the way of obtaining a uniform coating by the porosity of the ware, the biscuit surface must first be coated with varnish.

The material used in this operation is a quick-drying linseed varnish, prepared without the aid of lead compounds, owing to

their tendency to darken in colour after a time and thus impair the gloss of the colours.

This defect is absent in varnishes made with the aid of zinc or manganese compounds, and consequently these varnishes should be exclusively used for the purpose now in question.

The painting of the ware must not be commenced until the varnish is perfectly dry, and no longer feels tacky to the finger.

Owing to the low price of siderolith ware, hand-painting is rarely practised, being usually replaced by metachromotype transfers.

These are applied by moistening with oil of turpentine the side to be placed in contact with the ware, and then pressing it on to the surface of the latter. The oil of turpentine softens the layer of varnish sufficiently to cause the transfer to stick. After the oil of turpentine has evaporated, the cover paper is moistened with water until it has softened enough to be easily drawn off.

Before the transfer designs are applied, however, it is necessary to conceal the colour of the clay body entirely under a layer of coloured paint. By using zinc white for this purpose, the ware acquires the appearance of glazed white porcelain. The white can also be toned to ivory by a suitable admixture of yellow colouring matter; and the appearance of a coloured glaze can be imitated by using suitable colours.

The best way of drying the decorated ware is at ordinary temperature, the pieces being set up in a room free from dust, and left there until the colours have become so hard that they cannot be removed except by scraping with a cutting tool. Owing to the time occupied by this method of drying, however, some makers prefer to shorten the process by the use of artificial heat, generally in separate mufles. These must on no account be glowing, but merely hot. If the muffle temperature is too high, the residual traces of ethereal oil in

the colours will vaporise so rapidly as to form air-bells and cause the colour to moult, thus revealing the natural shade of the clay.

A better plan is to provide a drying-room, in which the ware is placed on racks and the air is warmed by means of a stove, the latter being fired from the outside, so as to prevent any access of dust or ash to the ware. When the room has been filled with ware, heat is applied, very slowly at first, so that the temperature is gradually raised to 85°–105° F.

After remaining at this temperature for several hours, it may be assumed that all the ethereal oil in the colour has evaporated, and the temperature may then be raised to 140° F. or over. When the colour on a test plate is found to have set so hard that it can only be removed by scraping it with a sharp knife, the drying is finished and the ware can be taken out, leaving the room ready for a fresh charge.

The dried ware is finally coated with another layer of varnish, a hard resin varnish being used for fine ware, since it increases the gloss, and hence the resemblance to glazed porcelain.

A specially handsome appearance is imparted by the skilful employment of bronze powders to produce metallic effects. This is particularly the case when the bronze is dabbed over a plain colour surface—red, green, or copper brown, etc.—by means of a brush or sponge.

However, to prevent the bronze changing colour after exposure to the air, a protecting cover of oil varnish must be applied. Such varnish must not contain free fatty acids, or these will soon form greenish compounds with the copper invariably present in the bronze powder: and a spirit amber or copal varnish must be used. The solvents—alcohol, wood spirit, acetone, etc.—in those varnishes are exceedingly volatile, and the varnish will dry very quickly, protecting the underlying bronze completely from the action of the air.

A process allied to the manufacture of siderolith ware, but chiefly adopted by amateurs, is the painting of earthenware on which the outlines of the various colours have already been marked.

Ware marked in this way is supplied by certain makers, ready fired, the contours of the ornamentation being shown in slight relief or intaglio. The designs are usually in the Persian or Indian style, and are filled up with different colours, the selection being a very wide one, since the colours are not exposed to any high temperature.

The colours must be sufficiently consistent to furnish, when applied with the brush, a stratum which will dry like a coloured glaze. These colours are generally incorporated with a medium of hard resin varnish containing sufficient soft resin varnish to prevent them from cracking or moulting when dry. The requisite softness is usually imparted to the amber or copal varnish by a small quantity of dammar varnish or copaiba balsam.

Gold and silver decorations are usually applied to this ware by attaching gold or silver leaf to a coating of golden yellow (or white) colour allowed to become nearly dry. A cheap silvery decoration is also made by mixing aluminium powder with a colourless varnish.

When the ware has been painted it should be coated with a thin film of Zapon lacquer, prepared by mixing ordinary collodion (an ethereal solution of gun-cotton) with about 4 per cent. of castor-oil. The thin film left by this varnish, after the ether has evaporated, is thoroughly waterproof, so that the varnished articles can be cleaned with a wet sponge or brush.

This varnish, however, must not be applied with a brush, being so volatile that it would dry under the brush itself; it must be poured over the article to be coated, and the latter allowed to drain. After leaving it untouched overnight, it

will be found perfectly dry, and will retain its fine gloss and handsome appearance permanently.

This method of decoration is latterly much used for imitating antique and costly vases, such as are found in museums, the imitations being used either for ornamental purposes in the home, or for the purpose of instruction in technical and art schools.

THE END.

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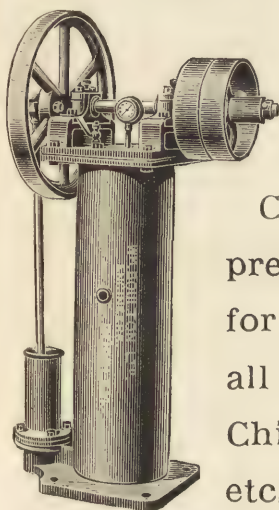
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